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# PATENT ABSTRACTS OF JAPAN

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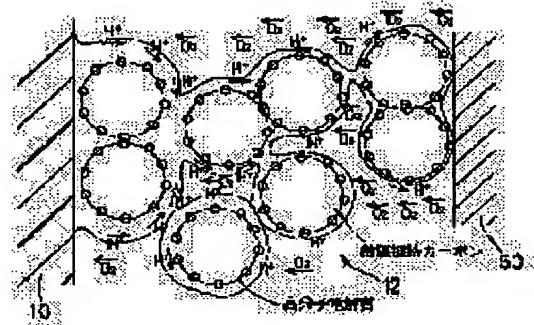
(21)Application number : 06-251390 (71)Applicant : TOYOTA MOTOR CORP  
 (22)Date of filing : 19.09.1994 (72)Inventor : KAWAHARA TATSUYA  
 MIZUNO SEIJI

## (54) FUEL CELL AND MANUFACTURE THEREOF

### (57)Abstract:

PURPOSE: To further enhance layer the battery performance.

CONSTITUTION: Electrode catalyst layer forming paste prepared by mixing a catalyst carrying carbon in a polymer electrolyte solution and an organic solvent is dripped on the surface of a Teflon sheet, and a paste printed material with uniform thickness is formed with a doctor blade. When the paste printed material stands within a sealed container, the catalyst carrying carbon is precipitated and stacked on the Teflon sheet. The polymer electrolyte solution is left as a supernatant liquid of the stacked layer. When a thin film is formed by drying, on the upper surface side of the film, the amount of the polymer electrolyte is increased and voids between the catalyst carrying carbon particles are made small, and on the bottom side of the film, the amount of the polymer electrolyte is decreased and the voids are made large. The film becomes an electrode catalyst layer formed by stacking the catalyst carrying carbon



particles, and the side having the large amount of polymer electrolyte is brought into close contact with an electrolyte film 10, and the side having large voids is brought into close contact with a cathode 50. The conductivity of hydrogen ions on the interface with the electrolyte film is enhanced, and the diffusion permeability of a reaction gas on the interface with an electrode is enhanced.

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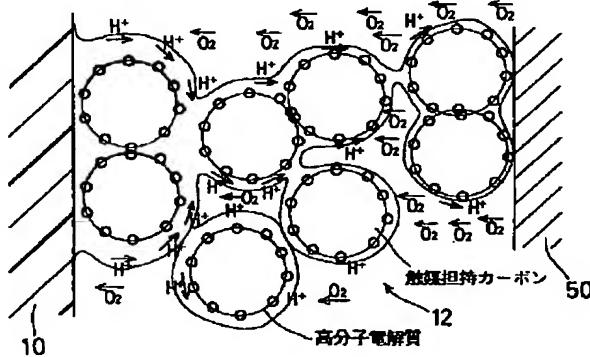
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(21) 出願番号	特願平6-251390	(71) 出願人	000003207 トヨタ自動車株式会社 愛知県豊田市トヨタ町1番地
(22) 出願日	平成6年(1994)9月19日	(72) 発明者	川原 竜也 愛知県豊田市トヨタ町1番地 トヨタ自動車株式会社内
		(72) 発明者	水野 誠司 愛知県豊田市トヨタ町1番地 トヨタ自動車株式会社内
		(74) 代理人	弁理士 下出 陸史 (外1名)

(54) 【発明の名称】 燃料電池とその製造方法

(57) 【要約】

【目的】 電池性能のより一層の向上を図る。  
【構成】 触媒担持カーボンを高分子電解質溶液と有機溶媒に混合して調製した電極触媒層形成用ペーストを、テフロンシート表面に滴下し、ドクターブレードにより均一厚さのペースト印刷物とする。このペースト印刷物を密閉容器内で静置すると、この静置の間に、触媒担持カーボンはテフロンシート上に沈降積層する。そして、積層の上澄みとして高分子電解質溶液が残る。これを乾燥を経て薄膜形成すると、膜の上面側では高分子電解質質量が多くて触媒担持カーボン間の空隙が小さくなり、膜の底面側では高分子電解質質量が少なくてこの空隙が大きくなる。この膜は、触媒担持カーボンが積層してなる電極触媒層となり、高分子電解質質量が多い側を電解質膜10と密着させ、空隙が大きい側をカソード50と密着させる。よって、電解質膜との界面での水素イオンの導電性を高め、電極との界面での反応ガスの拡散透過性を高める。



## 【特許請求の範囲】

【請求項1】 水素イオンの選択透過性を有する固体高分子電解質膜に触媒担持体を積層してなる電極触媒層を密着させ、該固体高分子電解質膜を該電極触媒層を介在させて一対のガス拡散性の電極で挟持した燃料電池であって、

前記電極触媒層は、水素イオンの選択透過性を有する高分子電解質で被覆した触媒担持体を積層してなり、前記電極触媒層における触媒担持体間の空隙は、前記触媒担持体を被覆する前記高分子電解質量を前記触媒担持体の積層方向に沿って変えることによって、前記固体高分子電解質膜側より前記電極側で大きくされていることを特徴とする燃料電池。

【請求項2】 請求項1記載の燃料電池の製造方法であって、

前記触媒担持体と前記高分子電解質溶液と揮発性の有機溶媒との混合溶液を準備する準備工程と、該混合溶液を薄膜状に延ばし、前記揮発性の有機溶媒が揮発しない環境に前記触媒担持体が沈降できる時間に亘って静置する静置工程と、前記薄膜状に延ばされた混合溶液から、乾燥処理を経て薄膜を形成する膜形成工程と、該形成された薄膜を、前記静置時に上面となっていた側の膜面が前記固体高分子電解質膜の膜面と接合するよう、前記固体高分子電解質膜に密着する密着工程とを備えることを特徴とする燃料電池の製造方法。

【請求項3】 請求項1記載の燃料電池の製造方法であって、

前記触媒担持体と前記高分子電解質溶液と揮発性の有機溶媒との混合溶液を準備する準備工程と、該混合溶液を、前記揮発性の有機溶媒が揮発しない環境に置かれて回転する回転容器に入れ込み、該入れ込まれた混合溶液に遠心力を及ぼして該混合溶液を薄膜状に延ばす薄膜化工程と、前記薄膜状に延ばされた混合溶液から、乾燥処理を経て薄膜を形成する膜形成工程と、該形成された薄膜を、前記回転容器の回転時に回転容器内で内側となっていた側の膜面が前記固体高分子電解質膜の膜面と接合するよう、前記固体高分子電解質膜に密着する密着工程とを備えることを特徴とする燃料電池の製造方法。

【請求項4】 請求項2又は請求項3記載の燃料電池の製造方法であって、

請求項2又は請求項3記載の準備工程は、粒径の異なる少なくとも二以上の触媒担持体と前記高分子電解質溶液と揮発性の有機溶媒との混合溶液を準備する工程である。

【請求項5】 請求項1記載の燃料電池の製造方法であって、

前記触媒担持体に対する前記高分子電解質量が異なる二

以上の混合溶液を、前記触媒担持体と前記高分子電解質溶液と揮発性の有機溶媒とを混合して準備する工程と、該二以上の混合溶液を用いて、前記触媒担持体に対する前記高分子電解質量が異なる二以上の薄膜を形成する工程と、

該形成された二以上の薄膜を、前記触媒担持体に対する前記高分子電解質量が多い順に前記固体高分子電解質膜に積層する工程とを備えることを特徴とする燃料電池の製造方法。

10 【請求項6】 触媒担持体を積層してなる電極触媒層とガス拡散性の電極とを密着させて一対ずつ備える燃料電池であって、

前記電極触媒層は、水素イオンの選択透過性を有する高分子電解質で被覆した触媒担持体を積層してなり、前記電極触媒層における触媒担持体間の空隙は、前記触媒担持体を被覆する前記高分子電解質量を前記触媒担持体の積層方向に沿って変えることによって、前記電極側で大きくされており、

前記一対の電極触媒層は、前記触媒担持体間の空隙が小さい側同士が密着するよう接合されていることを特徴とする燃料電池。

【請求項7】 請求項6記載の燃料電池の製造方法であって、

請求項2又は請求項3記載の準備工程と、

請求項2記載の静置工程又は請求項3記載の薄膜化工程のいずれかの工程と、

請求項2又は請求項3記載の膜形成工程と、

該形成された薄膜を一対用意する工程と、

該用意された一対の薄膜を前記静置工程において静置時に上面となっていた側の膜面同士を密着させて接合する接合工程か、該用意された一対の薄膜を前記薄膜化工程において回転容器内で内側となっていた側の膜面同士を密着させて接合する接合工程のいずれかの接合工程とを備えることを特徴とする燃料電池の製造方法。

【発明の詳細な説明】

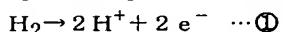
【0001】

【産業上の利用分野】 本発明は、水素イオンの選択透過性を有する固体高分子電解質膜に触媒担持体を電極触媒層を介在させて一対のガス拡散性の電極で挟持した燃料電池とその製造方法に関する。

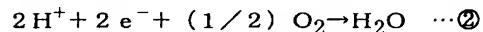
【0002】

【従来の技術】 この種の燃料電池では、固体高分子電解質膜を挟持する両電極においてその極性に応じて以下に記す反応式で示される電極反応を進行させ、電気エネルギーを得ている。

【0003】 アノード（水素極）：



【0004】 カソード（酸素極）：



【0005】 アノードで式①の反応により生成した水素

イオンは、 $H^+$  ( $xH_2O$ ) の水和状態で固体高分子電解質膜を透過（拡散）し、膜を透過した水素イオンは、カソードで式②の反応に供される。このアノードおよびカソードにおける電極反応は、固体高分子電解質膜に密着した電極触媒層を反応サイトとし、当該電極触媒層における触媒と固体高分子電解質膜との界面で進行する。

【0006】この触媒と固体高分子電解質膜との界面が増大し界面形成が均一化すれば、上記した①、②の反応がより円滑且つ活発に進行する。よって、この界面の増大と均一化を図るべく、特公表平5-507583では、電極触媒層を触媒担持カーボンがプロトン伝導性イオノマーに分散された状態のものとする技術が提案されている。なお、プロトン伝導性イオノマーは、固体高分子電解質膜と同一の機能である水素イオンの選択透過を発揮する高分子電解質溶液（ナフィオン溶液：ナフィオンは米国デュポン社の商品名）に外ならない。

【0007】この電極触媒層の形成には、触媒担持カーボンが高分子電解質溶液に分散された電極触媒層形成用ペーストが用いられる。つまり、この電極触媒層形成用ペーストを固体高分子電解質膜に直接塗布する、或いは、ペーストから膜成形して得たシートを固体高分子電解質膜にプレスすることで、固体高分子電解質膜に密着した電極触媒層が形成されている。これにより、電極触媒層における触媒の界面は、固体高分子電解質膜ばかりか高分子電解質とでも形成されるため、界面の増大と均一化が図られている。

#### 【0008】

【発明が解決しようとする課題】アノード、カソードにおける上記した①、②の反応の円滑化および活発化には、電極触媒層における触媒の界面の増大や界面形成の均一化のほかに、電極触媒層における反応ガスの拡散透過と水素イオンの導電が不可欠である。ところが、上記公報で提案された燃料電池では、電極触媒層において触媒担持カーボンが高分子電解質に平均的に分散されているため、次のような問題点が指摘されている。

【0009】触媒担持カーボンが高分子電解質に分散された電極触媒層では、高分子電解質は隣接する触媒担持カーボン間の隙間に介在し、触媒担持カーボンはこの高分子電解質によりバインドされたような状態で存在する。このため、電極触媒層における高分子電解質の量を増やせば、触媒担持カーボン間の隙間に介在する高分子電解質量が増大する。よって、電極触媒層における触媒担持カーボン間の空隙が小さくなり、反応ガスの拡散透過性は低下する。その反面、電極触媒層における水素イオンの導電性は、高分子電解質量が増えるほど高まる。一方、高分子電解質量を少なくすれば、触媒担持カーボン間の空隙が大きくなれば反応ガスの拡散透過性は高まる反面、水素イオンの導電性は低くなる。つまり、反応ガスの拡散透過性と水素イオンの導電性とは、背反する特性である。

【0010】電極触媒層において触媒担持カーボンを高分子電解質に平均的に分散されていた従来の燃料電池では、高分子電解質量の増減により上記したように反応ガスの拡散透過性と水素イオンの導電性とが変化する。このため、電極触媒層において好適な反応ガスの拡散透過性と水素イオンの導電性とを両立させることは困難であり、電池性能の向上の余地が残されている。

【0011】また、反応ガスの拡散透過性については、反応ガスをその流入箇所から速やかに拡散させる必要上、電極触媒層内側（固体高分子電解質膜側）より外側（ガス拡散電極側）で高いことが望ましい。一方、水素イオンの導電性については、水素イオンを速やかに固体高分子電解質膜に拡散させる都合上、ガス拡散電極側より固体高分子電解質膜側で高いことが望ましい。しかしながら、上記従来の燃料電池では、反応ガスの拡散透過性と水素イオンの導電性とは電極触媒層の内側から外側に亘ってそれぞれ一律となる。このため、反応ガスの拡散透過性と水素イオンの導電性とに層の内側と外側で高低をつけることができず、この点からも電池性能の向上の余地が残されている。換言すれば、層の内側から外側に亘って一律な反応ガスの拡散透過性により、ガス拡散電極側での反応ガスの拡散速度が制約される。一方、一律な水素イオンの導電性により、固体高分子電解質膜側での水素イオンの導電速度が制約される。このため、電極触媒層における触媒利用の効率が低く電池性能の更なる向上が阻害されていた。

【0012】本発明は、上記問題点を解決するためになされ、電池性能の更なる向上を図ると共に、高い電池性能を有する燃料電池の簡便な製造方法を提供することを目的とする。

【0013】

【課題を解決するための手段】かかる目的を達成するために請求項1記載の燃料電池の採用した手段は、水素イオンの選択透過性を有する固体高分子電解質膜に触媒担持体を積層してなる電極触媒層を密着させ、該固体高分子電解質膜を該電極触媒層を介在させて一対のガス拡散性の電極で挟持した燃料電池であって、前記電極触媒層は、水素イオンの選択透過性を有する高分子電解質で被覆した触媒担持体を積層してなり、前記電極触媒層における触媒担持体間の空隙は、前記触媒担持体を被覆する前記高分子電解質を前記触媒担持体の積層方向に沿って変えることによって、前記固体高分子電解質膜側より前記電極側で大きくされていることをその要旨とする。

【0014】そして、この請求項1記載の燃料電池を製造するために請求項2記載の製造方法で採用した手順は、前記触媒担持体と前記高分子電解質溶液と揮発性の有機溶媒との混合溶液を準備する準備工程と、該混合溶液を薄膜状に延ばし、前記揮発性の有機溶媒が揮発しない環境に前記触媒担持体が沈降できる時間に亘って静置する静置工程と、前記薄膜状に延ばされた混合溶液か

ら、乾燥処理を経て薄膜を形成する膜形成工程と、該形成された薄膜を、前記静置時に上面となっていた側の膜面が前記固体高分子電解質膜の膜面と接合するよう、前記固体高分子電解質膜に密着する密着工程とを備えることをその要旨とする。

【0015】また、請求項3記載の製造方法で採用した手順は、前記触媒担持体と前記高分子電解質溶液と揮発性の有機溶媒との混合溶液を準備する準備工程と、該混合溶液を、前記揮発性の有機溶媒が揮発しない環境に置かれて回転する回転容器に入れ込み、該入れ込まれた混合溶液に遠心力を及ぼして該混合溶液を薄膜状に延ばす薄膜化工程と、前記薄膜状に延ばされた混合溶液から、乾燥処理を経て薄膜を形成する膜形成工程と、該形成された薄膜を、前記回転容器の回転時に回転容器内で内側となっていた側の膜面が前記固体高分子電解質膜の膜面と接合するよう、前記固体高分子電解質膜に密着する密着工程とを備えることをその要旨とする。

【0016】この場合、請求項4記載の燃料電池の製造方法では、請求項2又は請求項3記載の準備工程を、粒径の異なる少なくとも二以上の触媒担持体と前記高分子電解質溶液と揮発性の有機溶媒との混合溶液を準備する工程とした。

【0017】また、請求項1記載の燃料電池を製造するために請求項5記載の製造方法で別途採用した手順は、前記触媒担持体に対する前記高分子電解質質量が異なる二以上の混合溶液を、前記触媒担持体と前記高分子電解質溶液と揮発性の有機溶媒とを混合して準備する工程と、該二以上の混合溶液を用いて、前記触媒担持体に対する前記高分子電解質質量が異なる二以上の薄膜を形成する工程と、該形成された二以上の薄膜を、前記触媒担持体に対する前記高分子電解質質量が多い順に前記固体高分子電解質膜に積層する工程とを備えることをその要旨とする。

【0018】また、上記目的を達成するために請求項6記載の燃料電池の採用した手段は、触媒担持体を積層してなる電極触媒層とガス拡散性の電極とを密着させて一対ずつ備える燃料電池であって、前記電極触媒層は、水素イオンの選択透過性を有する高分子電解質で被覆した触媒担持体を積層してなり、前記電極触媒層における触媒担持体間の空隙は、前記触媒担持体を被覆する前記高分子電解質質量を前記触媒担持体の積層方向に沿って変えることによって、前記電極側で大きくされており、前記一対の電極触媒層は、前記触媒担持体間の空隙が小さい側同士が密着するよう接合されていることをその要旨とする。

【0019】そして、この請求項6記載の燃料電池を製造するために請求項7記載の製造方法で採用した手順は、請求項2又は請求項3記載の準備工程と、請求項2記載の静置工程又は請求項3記載の薄膜化工程のいずれかの工程と、請求項2又は請求項3記載の膜形成工程

と、該形成された薄膜を一対用意する工程と、該用意された一対の薄膜を前記静置工程において静置時に上面となっていた側の膜面同士を密着させて接合する接合工程か、該用意された一対の薄膜を前記薄膜化工程において回転容器内で内側となっていた側の膜面同士を密着させて接合する接合工程のいずれかの接合工程とを備えることをその要旨とする。

【0020】

【作用】上記構成を有する請求項1記載の燃料電池で10は、電極触媒層における触媒担持体は、水素イオンの選択透過性を有する高分子電解質で被覆された状態で積層している。隣接する触媒担持体間では、触媒担持体回りの高分子電解質同士の接触がおきる。ところで、高分子電解質質量は触媒担持体の積層方向に沿って変えられているので、触媒担持体回りの高分子電解質同士の接触のおき具合も触媒担持体の積層方向に沿って変わることになる。その一方、触媒担持体回りの高分子電解質同士の接触のおき具合は、隣接する触媒担持体間の間隔を占める高分子電解質質量に反映する。よって、高分子電解質質量が20多ければ隣接する触媒担持体間の間隔を占める高分子電解質質量も増えて、触媒担持体間の空隙は小さくなり、高分子電解質質量が少なければ間隙を占める高分子電解質質量も少なくて、触媒担持体間の空隙は大きくなる。このため、請求項1記載の燃料電池では、高分子電解質質量を変えることで電極触媒層における触媒担持体間の空隙を固体高分子電解質膜側より電極側で大きくして、反応ガスの拡散透過性を電極側で高め、固体高分子電解質膜側で低くすることができる。一方、高分子電解質質量については、触媒担持体間の空隙とは逆に、電極側より固体高分子電解質膜側で多くなり、水素イオンの導電性を固体高分子電解質膜側で高めて電極側で低くすることができる。

【0021】請求項2記載の製造方法では、準備工程を経ることで、混合溶液中の触媒担持体の分散を通して、触媒担持体を高分子電解質溶液で覆われた状態とする。その後、静置工程を経ることで、膜状に延ばされた混合溶液において、触媒担持体を沈降させる。この沈降により、触媒担持体は、膜状に延ばされた混合溶液の底側に積層する。一方、高分子電解質溶液は、触媒担持体の積層においては触媒担持体を覆った状態で存在するものの、有機溶媒と共に積層の上澄みとしても存在する。

【0022】次いで、膜形成工程を経ることで、触媒担持体が積層してなる薄膜を形成する。つまり、膜形成工程の乾燥の処理の間に、混合溶液中の揮発性の有機溶媒と高分子電解質溶液の溶液分とを乾燥蒸発させる。これにより、高分子電解質溶液で覆われていた個々の触媒担持体は高分子電解質で被覆されると共に、この触媒担持体が積層した薄膜が形成される。この場合、静置工程において触媒担持体の積層の上澄みとして高分子電解質溶液を存在させるので、積層における上方の触媒担持体

は、この上澄みにおける高分子電解質溶液の高分子電解質により更に被覆される。つまり、触媒担持体の積層の上方、即ち静置時に上面となっていた側では、触媒担持体を被覆する高分子電解質質量が多くなる。よって、触媒担持体が積層してなる薄膜において、その底面側では高分子電解質質量が少なく、薄膜の上面側で高分子電解質質量が多くなる。このため、この薄膜では、高分子電解質質量が多い上面側（静置時に上面となっていた側）で、小さい触媒担持体間の空隙と高い水素イオンの導電性が発現し、高分子電解質質量が少ない底面側で、大きい触媒担持体間の空隙と低い水素イオンの導電性が発現する。

【0023】その後、密着工程を経ると、触媒担持体間の空隙が小さく高い水素イオンの導電性が発現した薄膜上面が固体高分子電解質膜の膜面と接合することになる。一方、水素イオンの導電性が低く大きな触媒担持体間の空隙が発現した薄膜底面は、一対のガス拡散性の電極での挟持を経て燃料電池が完成するとガス拡散性の電極側となる。

【0024】請求項3記載の製造方法では、準備工程を経ることで、触媒担持体を高分子電解質溶液で覆われた状態とする。その後、薄膜化工程を経ることで、回転容器において混合溶液に遠心力を及ぼし、この混合溶液を容器内壁に沿って膜状に延ばす。しかも、膜状に延ばされた混合溶液において、遠心力により触媒担持体を強制的に沈降させる。この沈降により、触媒担持体は、膜状に延ばされた混合溶液の底側（容器内壁側）に短時間のうちに積層する。一方、高分子電解質溶液は、触媒担持体の積層においては触媒担持体を覆った状態で存在するものの、有機溶媒と共に積層の上澄みとしても存在する。

【0025】次いで、膜形成工程を経ることで、請求項2記載の製造方法と同様、触媒担持体が積層してなる薄膜を形成する。つまり、膜形成工程の乾燥の処理の間の有機溶媒や高分子電解質溶液の溶液分の乾燥蒸発により、高分子電解質で被覆された触媒担持体が積層してなる薄膜を形成する。この場合、薄膜化工程においては、請求項2記載の静置工程と同様、触媒担持体の積層の上澄みとして高分子電解質溶液を存在させるので、触媒担持体の積層の上方、即ち回転容器での内側では、触媒担持体を被覆する高分子電解質質量を多くする。よって、触媒担持体が積層してなる薄膜において、その底面側では高分子電解質質量が少なく上面側で高分子電解質質量が多くなる。このため、この薄膜でも、請求項2記載の製造方法と同様、高分子電解質質量が多い上面側（回転容器での内側）で、小さい触媒担持体間の空隙と高い水素イオンの導電性が発現し、高分子電解質質量が少ない底面側で、大きい触媒担持体間の空隙と低い水素イオンの導電性が発現する。

【0026】その後、密着工程を経ると、触媒担持体間の空隙が小さく高い水素イオンの導電性が発現した薄

膜上面が固体高分子電解質膜の膜面と接合することになる。一方、水素イオンの導電性が低くて大きな触媒担持体間の空隙が発現した薄膜底面は、ガス拡散性の電極側となる。

【0027】請求項4記載の燃料電池の製造方法では、請求項2又は請求項3記載の準備工程において、粒径の異なる少なくとも二以上の触媒担持体を混合した混合溶液を準備することとした。よって、膜状に延ばされた混合溶液では、粒径の大きい触媒担持体が先に沈降し粒径が小さいほど遅く沈降する。このため、触媒担持体の積層は、触媒担持体の粒径に応じた積層部の積み重ねとなる。そして、各積層部では触媒担持体の粒径が異なることから、隣接する触媒担持体間の空隙が各積層部ごとで異なる。つまり、混合溶液の底側の積層部ほどこの割合が大きく底側から離れる積層部ほど小さくなる。

【0028】従って、その後の工程を経ることで、電極触媒層では、固体高分子電解質膜と接合する側で触媒担持体間の空隙が小さく水素イオンの導電性が高くなり、ガス拡散性の電極側でより水素イオンの導電性が低くて触媒担持体間の空隙が大きくなる。

【0029】請求項5記載の製造方法では、触媒担持体に対する高分子電解質質量が異なる二以上の混合溶液を準備し、この高分子電解質質量が異なる二以上の薄膜を形成する。そして、高分子電解質質量が多い順に、二以上の薄膜を固体高分子電解質膜に積層する。従って、固体高分子電解質膜側ほど高分子電解質質量が多くなるため、この製造方法でも、電極触媒層において、固体高分子電解質膜側で触媒担持体間の空隙が小さく水素イオンの導電性が高くなり、ガス拡散性の電極側でより水素イオンの導電性が低くて触媒担持体間の空隙が大きくなる。

【0030】また、請求項6記載の燃料電池にあっても、高分子電解質質量を触媒担持体の積層方向に沿って変えることで、請求項1記載の燃料電池と同様に、電極触媒層における触媒担持体間の空隙を電極側で大きくして、反応ガスの拡散透過性を電極側で高くその反対側で低くしている。一方、高分子電解質質量については、触媒担持体間の空隙とは逆に、電極側で小さくその反対側で大きくなり、水素イオンの導電性を電極側で低くその反対側で高くすることができる。そして、一対の電極触媒層は、触媒担持体間の空隙が小さい側同士、即ち高分子電解質質量が多くて水素イオンの導電性が高い側同士が密着するよう接合されている。よって、この高分子電解質質量が多くて水素イオンの導電性が高い側同士の密着領域は、燃料電池において、水素イオンの選択透過性を有する電解質膜として機能する。

【0031】請求項7記載の製造方法では、準備工程を経ることで、触媒担持体を高分子電解質溶液で覆われた状態とする。その後は、静置工程又は薄膜化工程のいずれかの工程を経ることで、膜状に延ばされた混合溶液において触媒担持体の沈降を図り、触媒担持体を、膜状に

延ばされた混合溶液の底側に積層させる。一方、高分子電解質溶液を、触媒担持体の積層においては触媒担持体を覆った状態で存在させ、積層の上には有機溶媒と共に上澄みとしても存在させる。

【0032】次いで、膜形成工程を経ることで、有機溶媒や高分子電解質溶液の溶液分の乾燥蒸発により、高分子電解質で被覆された触媒担持体が積層してなる薄膜を形成する。この場合、前工程において触媒担持体の積層の上澄みとして高分子電解質溶液を存在させるので、触媒担持体の積層の上方では、触媒担持体を被覆する高分子電解質量を多くする。よって、触媒担持体が積層してなる薄膜において、その底面側では高分子電解質量が少なく上面側で高分子電解質量が多くなる。このため、この薄膜でも、高分子電解質量が多い上面側で、小さい触媒担持体間の空隙と高い水素イオンの導電性が発現し、高分子電解質量が少ない底面側で、大きい触媒担持体間の空隙と低い水素イオンの導電性が発現する。

【0033】その後、いずれかの接合工程を経ると、高分子電解質量が多くて水素イオンの導電性が高い側同士が密着し、その密着領域は、燃料電池において、水素イオンの選択透過性を有する固体高分子電解質膜と同一の機能を果たす領域となる。また、高分子電解質量が多くて水素イオンの導電性が高い側と反対側は、水素イオンの導電性が低くて大きな触媒担持体間の空隙をもって、ガス拡散性の電極側と密着する。

#### 【0034】

【実施例】次に、本発明の構成・作用を一層明らかにするために、以下本発明の好適な実施例について説明する。図1は、この実施例における燃料電池（固体高分子型燃料電池）のセル構造の模式図である。

【0035】図示するように、セルは、膜状の電解質である電解質膜10と、この電解質膜10の膜面に密着したカソード側電極触媒層12およびアノード側電極触媒層14と、これら各電極触媒層に密着したカソード50およびアノード52とにより構成されている。

【0036】電解質膜10は、水素イオンに対するイオン交換基としてスルホン基を有する固体高分子電解質膜であり、水素イオンを膜厚方向に沿って選択的に透過する。具体的に説明すると、電解質膜10は、フッ素系スルホン酸高分子樹脂から作製された固体高分子電解質膜（例えばパーフルオロカーボンスルホン酸高分子膜（商品名：ナフィオン、DuPont社製））であり、その膜厚は120μm程度である。

【0037】カソード側電極触媒層12、アノード側電極触媒層14は、カソード50、アノード52と電解質膜10との間に介在し、これらのホットプレスを経ることで、電解質膜10の膜面および各電極の電解質側の電極表面に密着される。このカソード側電極触媒層12、アノード側電極触媒層14は、触媒として白金を20wt%担持したカーボン粒子が積層したものであり、後述

の製造工程を経て形成される。なお、図1においては、カソード側電極触媒層12、アノード側電極触媒層14を構成するカーボン粒子は誇張して描かれている。

【0038】カソード50、アノード52は、多孔質でガス透過性を有すると共に導電性のポーラスカーボンにより形成されており、その気孔率は60ないし80%である。また、カソード50およびアノード52には、対応する電極触媒層側にそれぞれ流路41が形成されている。なお、このカソード50およびアノード52は、ポーラスカーボンであることから、隣接する燃料電池セルを仕切るセパレータとしての機能をも果たす。

【0039】上記した構成の燃料電池は、各極に流路41、43から燃料ガス（加湿水素ガス、酸素ガス）が供給されると、供給された燃料ガスは、カソード50、アノード52を透過（拡散）して、カソード側電極触媒層12、アノード側電極触媒層14に到る。そして、その燃料ガスは、当該電極触媒層において、上述した式①、②に示す反応に供される。つまり、アノード52側では、式①の反応の進行により生成した水素イオンは、 $H^+$  ( $xH_2O$ ) の水和状態で電解質膜10を透過（拡散）し、膜を透過した水素イオンは、カソード50で式②の反応に供される。なお、この反応はカソード側電極触媒層12、アノード側電極触媒層14の触媒作用により促進して進行する。

【0040】次に、上記した燃料電池（セル）の製造工程について順を追って説明する。最初に、触媒担持カーボンと高分子電解質溶液と揮発性の有機溶媒との混合溶液を準備する準備工程について説明する。この準備工程では、まず、混合対象物を以下のように秤量する。つまり、白金（平均粒径約1nm）を20wt%担持した触媒担持カーボン（平均粒径約20nm）1gに対し、電解質膜10と同質のフッ素系スルホン酸高分子樹脂溶液（当該樹脂の固形分が5wt%で配合された溶液）を10ml1秤量する。更に、有機溶媒として、エチレングリコールモノイソプロピルエーテルおよびイソプロパノールをそれぞれ5mlずつ秤量する。なお、有機溶媒に限らず、前記の溶媒以外にもカーボンの分散が良好で電解質膜に悪影響を与えないものであればよい。

【0041】そして、必要なだけの量の触媒担持カーボン、フッ素系スルホン酸高分子樹脂溶液および有機溶媒をこの比率で用意する。次いで、用意した触媒担持カーボン等を密閉容器に入れ込み、この密閉容器内で触媒担持カーボンを超音波分散させる。こうして、準備工程が完了し電極触媒層を形成するための混合溶液、即ち電極触媒層形成用ペーストが調製される。この準備工程において、触媒担持カーボンは、フッ素系スルホン酸高分子樹脂溶液で覆われて溶液に分散した状態となる。

【0042】この場合、触媒担持カーボン1gに対するフッ素系スルホン酸高分子樹脂溶液の溶液量は、種々変更可能である。しかし、個々の触媒担持カーボンがフッ

素系スルホン酸高分子樹脂溶液におけるフッ素系スルホン酸高分子樹脂で被覆できる容量であることが必要である。

【0043】この準備工程に際して、用意した触媒担持カーボン等の原料のほか、密閉容器を予め冷却しておくことが望ましい。このように冷却しておくと、有機溶媒蒸気と空气中酸素とが白金触媒により反応してしまうことを防止できるからである。また、密閉容器を不活性ガスで置換する若しくは希薄酸素下におく等の処置も、有機溶媒蒸気の反応を防止する点で効果的である。更に、電極触媒層形成用ペーストのレオロジー特性に悪影響を与えない程度に、水やケトン、エステル等、酸素と反応しない溶媒を添加して混合しておくこともできる。なお、超音波分散に替えて、ホモジナイザ、ボールミル、遊星ミル等を用いた分散方法を探ることもできる。

【0044】その後は、以下の静置工程を行なう。つまり、まず前準備として、厚さ $300\mu\text{m}$ のテフロンシートを水平に維持された平面板の上面に固定し、テフロンシート表面をエタノールで洗浄する。次いで、上記調製済みの電極触媒層形成用ペーストをテフロンシート表面に滴下し、ドクターブレードにより $200\mu\text{m}$ の均一厚さで電極触媒層形成用ペーストを薄膜状に延ばしペースト印刷物を得る。この際、ドクターブレードのクリアランスを調節することで、種々の厚み、即ち種々の触媒量の電極触媒層を得ることができる。

【0045】次に、テフロンシート上のペースト印刷物を密閉容器内に載置し、24時間静置する。この静置の間に亘っては、密閉容器内は、電極触媒層形成用ペーストの有機溶媒と同一の有機溶媒が、その飽和蒸気圧で封入されている。よって、ペースト印刷物は、ペーストの有機溶媒が揮発しない環境下で静置されることになる。この静置の間に、電極触媒層形成用ペーストにおける触媒担持カーボンはペースト印刷物において沈降する。この沈降の様子を図2、図3に模式的に表わす。

【0046】つまり、静置前には、図2に示すようにペースト印刷物において分散していた触媒担持カーボンは、静置の間に沈降し、図3に示すようにペースト印刷物の底側に積層する。この場合、触媒担持カーボンの積層状態に極端な粗密は見られず、触媒担持カーボンはほぼ均一に分布して積層する。一方、フッ素系スルホン酸高分子樹脂溶液は、触媒担持カーボンの積層においては触媒担持カーボンを覆った状態で存在するものの、有機溶媒と共に積層の上澄みとしても存在する。なお、24時間の静置時間は、触媒担持カーボンがペースト印刷物において沈降するに十分な時間である。

【0047】次いで、ペースト印刷物を常温乾燥に付した後に $50^\circ\text{C}$ で真空乾燥に処して、膜形成工程を行なう。つまり、この真空乾燥により、ペースト印刷物からは、有機溶媒とフッ素系スルホン酸高分子樹脂溶液の溶液分とが乾燥蒸発して除去される。このため、この膜形

成工程を経ることで、フッ素系スルホン酸高分子樹脂溶液で覆われていた個々の触媒担持カーボンは高分子電解質であるフッ素系スルホン酸高分子樹脂で被覆されると共に、この触媒担持カーボンが積層した薄膜が形成される。この場合、静置工程において触媒担持カーボンの積層の上澄みとしてフッ素系スルホン酸高分子樹脂溶液は存在するので、積層における上方の触媒担持カーボンは、この上澄みにおけるフッ素系スルホン酸高分子樹脂溶液のフッ素系スルホン酸高分子樹脂により更に被覆される。なお、以下の説明にあっては、フッ素系スルホン酸高分子樹脂を単に高分子電解質という。

【0048】つまり、触媒担持カーボンの積層の上方、即ち静置時に上面となっていた側では、触媒担持カーボンを被覆する高分子電解質量が多くなる。よって、形成された薄膜において、その底面側では高分子電解質量が少なく、薄膜の上面側で高分子電解質量が多くなる。このため、この薄膜は、高分子電解質が多い膜上面側で小さい触媒担持カーボン間の空隙と高い水素イオンの導電性を備える。一方、高分子電解質量が少ない底面側で、大きい触媒担持カーボン間の空隙と低い水素イオンの導電性を備えることになる。

【0049】その後は、次のようにして燃料電池（セル）を完成された。まず、真空乾燥後のペースト印刷物をテフロンシートごと電解質膜10の両膜面に重ねてホットプレス（ $126^\circ\text{C} \times 100\text{kg/cm}^2$ ）し、このホットプレスの後にテフロンシートを除去する。次いで、この電解質膜10をカソード50、アノード52で挟持した状態で更にホットプレス（ $126^\circ\text{C} \times 100\text{kg/cm}^2$ ）した。上記した各工程を経て、電極触媒層形成用ペーストからカソード側電極触媒層12、アノード側電極触媒層14が形成されると共に、両電極触媒層を有する燃料電池（セル）が完成する。なお、ホットプレスに先立ちテフロンシートを除去し、ペースト印刷物を電解質膜10の両膜面に重ね、更にその両側をカソード50、アノード52で挟持した状態でホットプレスしてもよい。

【0050】こうして形成されたカソード側電極触媒層12、アノード側電極触媒層14における触媒担持カーボンと高分子電解質の存在の様子を、カソード側電極触媒層12を例に採り図をもって説明する。

【0051】カソード側電極触媒層12を模式的に表わした図4に示すように、各触媒担持カーボンは高分子電解質により被覆されている。しかし、触媒担持カーボン当たりの高分子電解質被覆量は、電解質膜10側で多くカソード50側で少ない。その一方、隣接する触媒担持カーボン間の間隙に高分子電解質が介在する介在量は電解質膜10側で多くカソード50側で少ない。このため、電極触媒層としての触媒担持カーボン間の空隙は、カソード50側で大きく電解質膜10側で小さい。よって、電解質膜10の膜面からカソード側電極触媒層12

への水素イオンの拡散は、カソード側電極触媒層12の電解質膜10側では高分子電解質量が多いことから速やかに行なわれる。しかも、カソード50からカソード側電極触媒層12への反応ガス（酸素ガス）の拡散透過は、カソード側電極触媒層12のカソード50側では触媒担持カーボン間の空隙が大きいことから速やかに行なわれる。

【0052】このため、カソード側電極触媒層12、アノード側電極触媒層14によれば、電解質膜10からの或いは電解質膜10への水素イオンの導電性を高めることができる。その反面、カソード50、アノード52側では、これら電極からの反応ガスの拡散透過性を高めることができる。

【0053】よって、本実施例の燃料電池では、電極触媒層において、カソード50、アノード52側で反応ガスの拡散速度を高め、電解質膜10側で水素イオンの導電速度を高めることができる。この結果、本実施例の燃料電池によれば、電極触媒層における触媒の利用効率を高めて電極反応をより円滑で活発にし、電池性能をより一層向上することができる。

【0054】次に、上記したカソード側電極触媒層12、アノード側電極触媒層14を有する本実施例（第1\*

サンプル区分	電流密度 (mA/cm <sup>2</sup> )				
	300	500	1000	1500	
電圧	比較例	1	0.80	0.80	放電不能
	第1実施例	1.04	0.94	0.72	0.48
	第2実施例	1.05	0.95	0.78	0.52
	第3実施例	1.04	0.95	0.77	0.58
	第4実施例	1.04	0.94	0.73	0.49
	第5実施例	1.05	0.96	0.79	0.62
	第6実施例	1.04	0.94	0.73	0.50

【0057】この表1における数値（データ）は、比較例燃料電池について、電流密度が300mA/cm<sup>2</sup>の場合に測定された電池電圧値を1とし、その他の燃料電池については、その測定値をこの電池電圧値で規格化した相対値で表示した。

【0058】この表1から明らかなように、第1実施例の燃料電池では、各電流密度について比較例燃料電池より高い電池電圧が得られた。特に、高い電流密度（1500mA/cm<sup>2</sup>）では、比較例燃料電池では放電ができず使用不能であるのに対して、第1実施例の燃料電池では、300mA/cm<sup>2</sup>の電流密度の場合のほぼ半分ではあるものの、電池電圧が得られた。よって、第1実施例の燃料電池では、高電流密度領域であっても、電極触媒層における触媒の利用効率を維持でき好ましい。

【0059】また、本実施例の製造工程によれば、ペースト印刷物を静置するという簡単な工程を探るだけで、高い電池性能を有する燃料電池を製造することができ

\*実施例）の燃料電池の性能評価について説明する。対比する比較例燃料電池（従来品）は、上記した実施例と同一の電池構成を備えるが、カソード側およびアノード側の電極触媒層の形成を静置工程を省略して行なった。つまり、比較例燃料電池では、第1実施例と同一の電極触媒層形成用ペーストからドクターブレードにより200μmの均一厚さでペースト印刷物を作製し、即座に薄膜して電解質膜10とホットプレスした。そして、両燃料電池について、I-V特性を調べた。その結果を表1に示す。なお、評価条件は、以下の通りである。また、この表1には、後述する第2ないし第6実施例における燃料電池の特性も載せられている。

【0055】電極面積：144cm<sup>2</sup>（12cm×12cm）；

セル温度：75°C；

反応ガス圧：アノード；水素0.2MPa（2ata），カソード；空気0.2MPa（2ata）；

ガス加湿方法：バーリング法（アノード水温90°C、カソード水温80°C）；

20 ガス利用率：アノード；50%，カソード；20%；

【0056】

【表1】

る。

【0060】次に、他の実施例（第2ないし第6実施例）について順次説明する。

【0061】第2実施例では、準備工程で準備した混合溶液（電極触媒層形成用ペースト）における触媒担持カーボンを以下のものとした点で上記した第1実施例と相

40 違し、燃料電池セル構造等は第1実施例と同一である。

【0062】この第2実施例では、準備工程において、平均粒径約1nmの白金を20wt%担持した第1のファーネスブラック（平均粒径約20nm）と平均粒径約2nmの白金を20wt%担持した第2のファーネスブラック（平均粒径約40nm）とを1:1の比率で配合した混合ファーネスブラックを用意し、第1実施例と同じフッ素系スルホン酸高分子樹脂溶液と有機溶媒とで、電極触媒層形成用ペーストを調製した。この場合、混合ファーネスブラック1gに対するフッ素系スルホン酸高分子樹脂溶液と各有機溶媒の秤量量は、第1実施例と同

一である。つまり、この第2実施例では、粒径が異なる2種類の触媒担持体（第1、第2のファーネスブラック）が分散した電極触媒層形成用ペーストを調製し、その後は第1実施例と同一の工程（静置工程、膜形成工程等）を経て燃料電池を製造した。

【0063】この場合、第2実施例の静置工程では、電極触媒層形成用ペーストで得られたペースト印刷物において、粒径の大きい第2のファーネスブラックが先に沈降し、粒径が小さい第1のファーネスブラックは遅く沈降する。このため、ペースト印刷物の底面側に第2のファーネスブラックの積層部ができ、その上に第1のファーネスブラックの積層部が積み重なる。そして、各積層部ではファーネスブラックの粒径が異なることから、隣接するファーネスブラックの空隙は、第2のファーネスブラックの積層部で大きく、第1のファーネスブラックの積層部で小さくなる。

【0064】しかも、この第2実施例でも、ファーネスブラックの積層の上澄みとしてフッ素系スルホン酸高分子樹脂溶液は存在する。このため、第1のファーネスブラックの積層部側では、ファーネスブラックを被覆する高分子電解質量が多くなり、底面側の第2のファーネスブラックの積層部側では、高分子電解質量が少なくなる。そして、その後の工程を経ることで、ペースト印刷物の上面側の第1のファーネスブラックの積層部が電解質膜10に密着し、底面側の第2のファーネスブラックの積層部が該当する電極に密着する。よって、この第2実施例にて形成された電極触媒層における第1、第2のファーネスブラックと高分子電解質の存在の様子は、次のようになる。

【0065】即ち、カソード側電極触媒層12を例に探って模式的に示す図5に示すように、第1、第2のファーネスブラックは高分子電解質により被覆されている。しかし、ファーネスブラック当たりの高分子電解質被覆量は、電解質膜10側で多くカソード50側で少ない。その一方、隣接するファーネスブラック間の間隙に高分子電解質が介在する介在量は、電解質膜10側で多くカソード50側で少なくなるので、電極触媒層としての触媒担持カーボン間の空隙は、カソード50側で大きく電解質膜10側で小さい。よって、電解質膜10の膜面からカソード側電極触媒層12への水素イオンの拡散は、カソード側電極触媒層12の電解質膜10側では高分子電解質量が多いことから速やかに行なわれる。しかも、カソード50からカソード側電極触媒層12への反応ガス（酸素ガス）の拡散透過は、カソード側電極触媒層12のカソード50側では触媒担持カーボン間の空隙が大きいことから速やかに行なわれる。

【0066】このため、第2実施例の燃料電池におけるカソード側電極触媒層12、アノード側電極触媒層14によっても、カソード50、アノード52側で反応ガスの拡散速度を高め、電解質膜10側で水素イオンの導電

速度を高めることができる。この結果、この第2実施例の燃料電池でも、電極触媒層における触媒の利用効率を高めて電極反応をより円滑で活発にし、電池性能をより一層向上することができる。

【0067】そして、表1における第2実施例の燃料電池についてのデータから明らかのように、第2実施例の燃料電池によっても、各電流密度について比較例燃料電池より高い電池電圧が得られると共に、高電流密度領域であっても、電極触媒層における触媒の利用効率を維持できた。

【0068】また、この第2の実施例においては、触媒担持カーボンの粒径を変えることによっても触媒担持カーボン粒子間の空隙の大きさを変えているが、触媒担持カーボンの粒子自体は、略均一に分布している。このため、上記した第1の実施例に比較して高電流密度領域での電圧降下を小さくすることができる。

【0069】次に、第3実施例について説明する。この第3実施例では、電極触媒層形成用ペーストに用いる触媒担持体の種類が上記の第2実施例と相違し、燃料電池20セル構造等はやはり第1実施例と同一である。

【0070】この第3実施例では、準備工程において、ファーネスブラックとアセチレンブラックとを用いた。そして、平均粒径約1nmの白金を20wt%担持したファーネスブラック（平均粒径約20nm）と平均粒径約3nmの白金を20wt%担持したアセチレンブラック（平均粒径約40nm）とを1:1の比率で配合して、電極触媒層形成用ペーストを調製した。

【0071】この第3実施例の静置工程においても、粒径の大きいアセチレンブラックが先に沈降し、粒径が小さいファーネスブラックは遅く沈降する。このため、ペースト印刷物の底面側にアセチレンブラックの積層部ができ、その上にファーネスブラックの積層部が積み重なる。そして、ペースト印刷物の上面側のファーネスブラックの積層部が電解質膜10に密着し、底面側のアセチレンブラックの積層部が該当する電極に密着する。よって、第2実施例と同様に、電極触媒層の電解質膜側では高分子電解質量が多くて触媒担持カーボン間の空隙が小さく、電極側で高分子電解質量が少なくて触媒担持カーボン間の空隙が大きくなる。従って、第3実施例の燃料40電池でも、電極触媒層における触媒の利用効率を高めて電極反応をより円滑で活発にし、電池性能をより一層向上することができる。

【0072】また、表1における第3実施例の燃料電池についてのデータから明らかのように、第3実施例の燃料電池によっても、各電流密度について比較例燃料電池より高い電池電圧が得られると共に、高電流密度領域であっても、電極触媒層における触媒の利用効率を維持できた。

【0073】この第3実施例では、電極触媒層の電極（カソード50、アノード52）に密着する側に、触媒

担持体としてアセチレンブラックを用いた。このアセチレンブラックは、表面官能基が少なく大きな疎水性を有する。よって、第3実施例の燃料電池では、カソード側電極触媒層12、アノード側電極触媒層14に電極側で疎水性を付与することができる。このため、次のような利点がある。

【0074】カーボン表面が強い親水性を示す場合、高分子電解質とカーボン表面との間に水が溜まり易い傾向がある。これは、高分子電解質の含水率を上げ、導電性を向上させることには効果があるが、過剰な水分、具体的には過剰な生成水がある場合には、水の相が高分子電解質との界面にできてしまい、触媒へのガス拡散を阻害する。逆に、カーボン表面が疎水性を示す場合には、高分子電解質との界面では水が保持され難くなり、ガス拡散性の向上を得やすい。このため、第3の実施例においては、電極触媒層におけるフラディングを抑制することができ、第2の実施例に比較して更に高電流密度領域での出力電圧の降下を小さくすることができる。

【0075】次に、第4実施例について説明する。この第4実施例では、第1実施例における静置工程に替えて、以下に説明する薄膜化工程を採った点で第1実施例と相違し、燃料電池セル構造等や準備工程における電極触媒層形成用ペーストの組成は第1実施例と同一である。

【0076】この第4実施例で採用した薄膜化工程では、第1実施例における準備工程で調製した電極触媒層形成用ペーストから、薄膜形成装置を用いて薄膜を形成する。ここで、薄膜化工程の説明に先立ち、当該工程に用いる薄膜形成装置20について説明する。

【0077】薄膜形成装置20は、その概略構成を表わした図6に示すように、中心軸を中心回転する中空の筒状回転容器22を備え、その側壁には、筒状回転容器22内を加熱するヒータ24が埋設されている。また、筒状回転容器22の内周壁には、厚さ300μmのテフロンシート26が周壁に沿って固定されている。このテフロンシート26は、筒状回転容器22の内周壁に取り外し自在であり、取付前にはその表面がエタノールで洗浄される。また、筒状回転容器22の下端中央には、有機溶媒蒸気や電極触媒層形成用ペーストの導入口28が設けられている。一方、上端中央には、筒状回転容器22内を吸引する吸引口30が設けられており、この吸引口30は図示しない真空吸引装置に接続されている。なお、筒状回転容器22の上端面は、開閉できるよう構成されている。

【0078】この薄膜形成装置20を用いた薄膜化工程では、まず、導入口28から電極触媒層形成用ペーストの有機溶媒と同一の有機溶媒を導入し、筒状回転容器22内を飽和蒸気圧の有機溶媒で満たす。これにより、筒状回転容器22内は、電極触媒層形成用ペーストが導入されても、ペーストにおける有機溶媒が揮発しない環境

となる。そして、この筒状回転容器22を回転させつつ導入口28から電極触媒層形成用ペースト32を導入し、筒状回転容器22を、20G (Gは重力加速度) の遠心力がかかる回転速度で20分間回転する。この筒状回転容器22の回転の間に、電極触媒層形成用ペースト32は、遠心力を受けて筒状回転容器22内周壁のテフロンシート26に沿って膜状に延ばされる。そして、電極触媒層形成用ペースト32における触媒担持カーボンは、やはりこの遠心力を受け、強制的にテフロンシート26側に沈降する。この強制的な沈降により、触媒担持カーボンは、テフロンシート26側に短時間のうちに積層し、筒状回転容器22の回転軸側は、フッ素系スルホン酸高分子樹脂溶液の存在する上澄みとなる。つまり、この薄膜化工程により、図3に示す第1実施例の静置工程での触媒担持カーボンの沈降が速やかに起こる。

【0079】その後、筒状回転容器22の回転を継続し、その間にヒータ24により筒状回転容器22内を50℃に加熱すると共に、吸引口30を介して筒状回転容器22内を真空吸引する。つまり、筒状回転容器22の高速回転させてペーストを膜状とする薄膜化工程に統いて、真空乾燥を有する膜形成工程を行なう。この薄膜工程は、筒状回転容器22の回転中に真空乾燥を行なう点で第1実施例の薄膜工程と相違するに過ぎない。この薄膜工程に統いては、第1実施例と同様の工程を経る。しかし、ホットプレスを経た電解質膜10との密着に際しては、筒状回転容器22の回転中にその回転軸側に位置していた側の膜面が、電解質膜10と密着される。

【0080】従って、この第4実施例の燃料電池であっても、第1実施例と同様に、電極触媒層の電解質膜側では高分子電解質量が多くて触媒担持カーボン間の空隙が小さく、電極側で高分子電解質量が少なくて触媒担持カーボン間の空隙が大きくなる。このため、第4実施例の燃料電池でも、電極触媒層における触媒の利用効率を高めて電極反応をより円滑で活発にし、電池性能をより一層向上することができる。

【0081】また、表1における第4実施例の燃料電池についてのデータから明らかのように、この第4実施例の燃料電池によつても、各電流密度について比較例燃料電池より高い電池電圧が得られると共に、高電流密度領域であつても、電極触媒層における触媒の利用効率を維持できた。

【0082】更に、この第4実施例では、遠心力により触媒担持カーボンの沈降を強制的に行なうので、短時間のうちに沈降を完了させる。よつて、第4実施例の製造工程によれば、筒状回転容器22内にて遠心力を及ぼすという簡便な工程を探るだけで、高い電池性能を有する燃料電池を短時間のうちに製造することができる。しかも、触媒担持カーボンの沈降を遠心力により行なうので、調製の困難なペーストのレオロジーに左右されることがなくこの沈降を起こすことができる。よつて、ペース

トのレオロジーの調製が不要となり、製造工程の簡略化を図ることができる。加えて、第4実施例の製造工程によれば、筒状回転容器22内周壁のテフロンシート26に沿って形成された電極触媒層形成用ペースト32の薄膜の均一化を通して、カソード側電極触媒層12、アノード側電極触媒層14の厚みの均一化も達成できる。また、電極触媒層形成用ペーストの歩留まりの向上をも図ることができる。

【0083】次に、第5実施例の燃料電池について説明する。この第5実施例の燃料電池では、その製造工程の準備工程において、過剰のフッ素系スルホン酸高分子樹脂溶液と有機溶媒を用いた電極触媒層形成用ペーストを調製する点と、独立した構成部材としての電解質膜10を用いない点で第4実施例と異なる。

【0084】つまり、この第5実施例の準備工程では、白金（平均粒径約1nm）を20wt%担持した触媒担持カーボン（平均粒径約20nm）1gに対し、フッ素系スルホン酸高分子樹脂溶液（当該樹脂の固形分が5wt%で配合された溶液）を150mL、有機溶媒としてプロピレングリコールを100mL秤量する。そして、必要なだけの量の触媒担持カーボン、フッ素系スルホン酸高分子樹脂溶液および有機溶媒をこの比率で用意し、フッ素系スルホン酸高分子樹脂溶液が過剰の電極触媒層形成用ペーストを調製した。

【0085】その後は、第4実施例と同様に、薄膜形成装置20を用いた薄膜化工程と膜形成工程とを行ない、電極触媒層形成用ペーストから薄膜を形成した。この場合、薄膜化工程では、筒状回転容器22を30Gの遠心力がかかる回転速度で120分間回転させた。この第5実施例では、薄膜化工程の間に膜状に延ばされたペーストにおいて、触媒担持カーボンの積層の上に多量の上澄みが残り、この状態で膜形成工程を経て薄膜を形成した。なお、膜形成工程においては、100°Cで真空乾燥を行なった。

【0086】こうして形成された薄膜であっても、薄膜化工程の際のテフロンシート側で高分子電解質が少なくて触媒担持カーボン間の空隙が大きくなる。また、テフロンシート側から離れるに従って高分子電解質が多くて触媒担持カーボン間の空隙が小さくなる。そして、テフロンシートと反対側（筒状回転容器22の回転軸側）では、触媒担持カーボンの積層の上に、フッ素系スルホン酸高分子樹脂（高分子電解質）のみの領域が形成される。

【0087】第5実施例では、薄膜化工程、膜形成工程を経た後に次の工程を行なう。まず、薄膜化工程、膜形成工程を経て上記の電極触媒層形成用ペーストから形成された薄膜を2枚用意する。そして、この2枚の薄膜を、高分子電解質のみの領域が形成され側の膜面同士を密着させてホットプレス（126°C×100kg/cm<sup>2</sup>）する。こうして、触媒担持カーボンが積層した電極

触媒層を両側に有する電極触媒構造体を得た。この電極触媒構造体では、その中央に、高分子電解質のみの領域が接合した約50μmのキャスト膜が形成された。その後は、テフロンシートを除去し、カソード50とアノード52で電極触媒構造体を挟持してこれらを一体化させ燃料電池を完成させた。

【0088】この第5実施例の燃料電池では、電極触媒構造体中央で高分子電解質のみの領域が接合してなるキャスト膜が約50μmの厚みを有することから、このキャスト膜を電解質膜10の代用として用いることができる。しかも、上記した各実施例と同様に、電極側では高分子電解質が少なくて触媒担持カーボン間の空隙が大きくなり、キャスト膜側では高分子電解質が多くて触媒担持カーボン間の空隙が小さくなる。従って、この第5実施例の燃料電池であっても、上記した各実施例と同様に、電極触媒層における触媒の利用効率を高めて電極反応をより円滑で活発にし、電池性能をより一層向上することができる。

【0089】この第5の実施例の燃料電池においては、20電解質膜に相当するキャスト膜が薄膜に形成されているので、電解質膜としての抵抗値を下げることができる。このため、第5の実施例の燃料電池では、更に高電流密度領域での出力電圧の低下を抑制することができる。

【0090】また、表1における第5実施例の燃料電池についてのデータから明らかなように、この第5実施例の燃料電池によっても、各電流密度について比較例燃料電池より高い電池電圧が得られると共に、高電流密度領域であっても、電極触媒層における触媒の利用効率を維持できた。

【0091】更に、この第5実施例では、電極触媒構造体中央のキャスト膜を電解質膜10の代用として用いるので、電解質膜10を個別に用意する必要がない。このため、第5実施例では、燃料電池の構成ばかりか、その製造工程をも簡略化することができる。

【0092】次に、第6実施例の燃料電池について説明する。この第6実施例の燃料電池では、燃料電池セル構造は第1実施例と同一である。しかし、カソード側電極触媒層12、アノード側電極触媒層14がそれぞれ第1～第3の触媒層が積層した3層構造である点で上記した40第1実施例と相違する。このような3層構造の電極触媒層を有する第6実施例の燃料電池は、以下の製造工程を経て製造される。

【0093】まず、第1触媒層を形成するための第1触媒層形成用ペーストを調製する。即ち、白金（平均粒径約1nm）を20wt%担持した触媒担持カーボン（平均粒径約20nm）1gに対し、フッ素系スルホン酸高分子樹脂溶液（当該樹脂の固形分が5wt%で配合された溶液）を15mL秤量する。更に、有機溶媒として、エチレングリコールモノイソプロピルエーテルおよびイソプロパノールをそれぞれ5mLずつ秤量する。そし

て、これら原料の密閉容器中での超音波分散を経て第1触媒層形成用ペーストを調製する。同様に、第2触媒層形成用ペーストと第3触媒層形成用ペーストとを調製する。この際、第2触媒層形成用ペーストでは、触媒担持カーボン1gに対してフッ素系スルホン酸高分子樹脂溶液が10ml、第3触媒層形成用ペーストでは、触媒担持カーボン1gに対してフッ素系スルホン酸高分子樹脂溶液が5ml秤量され、有機溶媒については第1触媒層形成用ペーストと同量である。つまり、第1～第3の触媒層の形成のためのそれぞれのペーストでは、触媒担持カーボンに対するフッ素系スルホン酸高分子樹脂溶液量が異なり、第1触媒層形成用ペースト、第2触媒層形成用ペースト、第3触媒層形成用ペーストの順にフッ素系スルホン酸高分子樹脂溶液量が少なくなる。

【0094】次に、上記調製したそれぞれのペーストから、第1実施例と同様に、テフロンシート上にドクターブレードにより均一厚さのペースト印刷物を得る。この場合、第1触媒層形成用ペーストと第3触媒層形成用ペーストからのペースト印刷物では、その厚さを50μmとし、第2触媒層形成用ペーストからのペースト印刷物では、100μmとした。この得られたペースト印刷物では、第1触媒層形成用ペースト、第2触媒層形成用ペースト、第3触媒層形成用ペーストの順にペースト印刷物におけるフッ素系スルホン酸高分子樹脂量（高分子電解質量）が少なくなる。

【0095】その後は、得られたそれぞれのペースト印刷物を即座に常温乾燥に付して50℃で真空乾燥に処する。これにより、高分子電解質であるフッ素系スルホン酸高分子樹脂で被覆された触媒担持カーボンが積層した薄膜がそれぞれ形成される。次いで、それぞれの薄膜を、触媒担持カーボンに対するフッ素系スルホン酸高分子樹脂量が多い順に電解質膜10に積層する。つまり、まず最初に、第1触媒層形成用ペーストからペースト印刷物を経て形成された薄膜を電解質膜10に密着してホットプレス（126℃×100kg/cm<sup>2</sup>）する。次に、このプレス済みの薄膜からテフロンシートを除去し、シート除去後の薄膜に、第2触媒層形成用ペーストから形成済みの薄膜を密着してホットプレスする。同様に、シート除去後の薄膜に、第3触媒層形成用ペーストから形成済みの薄膜を密着してホットプレスする。

【0096】これにより、それぞれの薄膜が第1～第3の触媒層となり、これらが積層した3層構造の電極触媒層（カソード側電極触媒層12、アノード側電極触媒層14）が形成される。そして、この両電極触媒層にカソード50、アノード52をプレスしてこれらを一体化し、燃料電池（セル）を完成させた。なお、上記したそれぞれの薄膜は、ホットプレスに先立ち予め電極サイズに裁断される。

【0097】この第6実施例の燃料電池では、第1、第2、第3の触媒層の順に高分子電解質量が少なくなつて

いる。よって、上記した各実施例と同様に、電解質膜側の第1の触媒層では高分子電解質量が多くて触媒担持カーボン間の空隙が小さく、電極側の第3の触媒層で高分子電解質量が少なくて触媒担持カーボン間の空隙が大きくなる。このため、第6実施例の燃料電池でも、電極触媒層における触媒の利用効率を高めて電極反応をより円滑で活発にし、電池性能をより一層向上することができる。

【0098】また、表1における第6実施例の燃料電池10についてのデータから明らかなように、この第6実施例の燃料電池によつても、各電流密度について比較例燃料電池より高い電池電圧が得られると共に、高電流密度領域であつても、電極触媒層における触媒の利用効率を維持できた。

【0099】以上本発明の実施例について説明したが、本発明はこの様な実施例になんら限定されるものではなく、本発明の要旨を逸脱しない範囲において種々なる態様で実施し得ることは勿論である。

【0100】例えば、上記した第4実施例における薄膜化工程で使用する電極触媒形成用ペーストを第2、第3実施例で使用した電極触媒形成用ペースト、即ち異なる粒径の触媒担持体を混合・分散したペーストとしてもよい。このように構成することで、電極触媒層、延いては燃料電池の製造時間を短縮することができる。

【0101】また、第5実施例において、電極触媒形成用ペーストに通常の触媒担持カーボン（平均粒径20～40μm）よりその平均粒径が小さい触媒担持カーボン、例えば白金触媒を担持しその平均粒径が1～5μmの触媒担持カーボンを少量配合するよう構成してもよい。このように構成した場合には、薄膜化工程においては、この微細粒径の触媒担持カーボンの沈降は通常の触媒担持カーボンより遅延しておきる。つまり、通常の触媒担持カーボンの沈降完了後にも、微細粒径の触媒担持カーボンは沈降の過程にある。このため、電極触媒構造体中央のキャスト膜を微細粒径の触媒担持カーボンが少量残留したキャスト膜とすることができます。

【0102】よつて、カソード50又はアノード52から対向する電極側に燃料ガスがクロスリークしてきても、この燃料ガスをキャスト膜中の微細粒径の触媒担持カーボンにおける触媒により電極触媒構造体で電極反応に供することができる。従つて、燃料ガス同士の反応（水素と酸素の反応）が電極触媒構造体で起きることを回避でき、キャスト膜の不用意な熱損傷を防止することができる。また、電極反応により生成する生成水によりこのキャスト膜を潤滑化することができ、当該膜の水素イオン拡散を阻害することがない。

【0103】また、第6実施例では、電極触媒層を第1、第2、第3の触媒層を積層した3層構造としたが、2層構造或いは4層以上の構造とすることもできる。

【0104】更に、上記した各実施例では、電極触媒層

形成用ペーストの調製の際に触媒担持カーボンをただ単にフッ素系スルホン酸高分子樹脂溶液（高分子電解質溶液）と有機溶媒に混合しこれらを超音波分散させた。しかし、一般にカーボンは疎水性を有し、フッ素系スルホン酸高分子樹脂は自身のスルホン基により親水性を有する。このため、超音波分散が不十分であったりすると、互いの性質により触媒担持カーボンはカーボン同士で凝集して、触媒担持カーボンのフッ素系スルホン酸高分子樹脂被覆（高分子電解質被覆）が不十分となる虞がある。よって、高分子電解質による触媒担持カーボンの確実な被覆を図るために、以下のようにして電極触媒層形成用ペーストを調製することが好ましい。

【0105】例えば、高分子電解質溶液に混合させる触媒担持カーボンを、その表面芳香族環に塩基性の官能基が結合したカーボンとしたり、正電荷に帶電したカーボンとする。このようにすれば、次のような理由から、触媒担持カーボン同士の凝集は起きないので、高分子電解質による触媒担持カーボンの確実な被覆を図ができる。

【0106】表面芳香族環に塩基性の官能基が結合した触媒担持カーボンでは、その表面芳香族環に結合した塩基性の官能基が溶液中において陽イオンに変遷する。このため、触媒担持カーボン同士は、電気的に反発しあい高分子電解質溶液中で凝集することは少なくなる。しかも、高分子電解質は水素イオン（陽イオン）に対して陰性のイオン交換基（例えばスルホン基）を有するので、触媒担持カーボンは高分子電解質と電気化学的に引き合う。この結果、表面芳香族環に塩基性の官能基が結合した触媒担持カーボンを用いて調製した電極触媒層形成用ペーストでは、個々の触媒担持カーボンは確実に高分子電解質にて被覆される。

【0107】一方、正電荷に帶電させた触媒担持カーボンは、その帶電電荷により互いに電気的に反発しあい凝集することは少なくなる。そして、陰性のイオン交換基を有する高分子電解質と電気化学的に引き合う。この結果、正電荷に帶電させた触媒担持カーボンを用いて調製した電極触媒層形成用ペーストであっても、個々の触媒担持カーボンは確実に高分子電解質にて被覆される。

【0108】そして、このような触媒担持カーボンを用いれば、個々の触媒担持カーボンが高分子電解質で確実に被覆されていることから、高分子電解質の変化を通してより確実に、電極側では反応ガスの拡散透過性を高く電解質膜側では水素イオンの導電性を高くできる。

【0109】なお、触媒担持カーボンの表面芳香族環への塩基性の官能基の結合は、次のようにして行なえばよい。まず、触媒担持カーボン粒子を、硝酸（ $\text{HNO}_3$ ）で加熱処理して（加熱温度：約400°C）、カーボンの表面芳香族環をニトロ化（ $-\text{NO}_2$ ）する。次いで、ニッケルを還元触媒として用い、このニトロ基（ $-\text{NO}_2$ ）を水素で還元してアミノ基（ $-\text{NH}_2$ ）に置換す

る。こうして、触媒担持カーボンの表面芳香族環に塩基性の官能基であるアミノ基（ $-\text{NH}_2$ ）が結合される。このアミノ基（ $-\text{NH}_2$ ）は、溶液中においてイオン化し陽イオン（アンモニウムイオン）に変遷する。

【0110】また、触媒担持カーボンへの正電荷の帶電は、図7に示すペースト調製装置60を用いて、次のようにして行なえばよい。まず、触媒担持カーボン粒子を、ペースト調製装置60の正電荷帶電室62に入れ込む。ここで、正電荷の帶電の説明に先立ち、ペースト調製装置60について説明する。

【0111】ペースト調製装置60は、誘電体64を挟んで正電荷帶電室62と負電荷帶電室66とを備える。そして、各帶電室の電極板62a, 66aには、スイッチ68が閉じられると、直流電源70の電荷を受けて正・負の電荷がかかる。正電荷帶電室62は、密閉されており、触媒担持カーボンやフッ素系スルホン酸高分子樹脂溶液を入れ込むための入り口バルブ62bと、封入物を排出するための排出バルブ62cを有する。

【0112】触媒担持カーボンを入り口バルブ62bから正電荷帶電室62に入れ込んだ後には、スイッチ68を閉じて正電荷帶電室62内の電極板62aを正電荷をかける。これにより、正電荷帶電室62において触媒担持カーボンは正電荷に帶電される。

【0113】こうして触媒担持カーボンが正電荷に帶電している状態で、入り口バルブ62bから高分子電解質溶液と有機溶媒をそれぞれ入れ込む。そして、図示しない超音波ホーンから正電荷帶電室62に超音波を放射して、正電荷が帶電した触媒担持カーボンを高分子電解質溶液に超音波分散させる。

【0114】【発明の効果】以上詳述したように請求項1および請求項6記載の燃料電池では、電極触媒層における触媒担持体間の空隙を電極側で大きくして反応ガスの拡散透過性を電極側で高くし、高分子電解質を電極と反対側の固体高分子電解質膜側で多くして水素イオンの導電性を固体高分子電解質膜側で高くした。よって、電極触媒層では、電極側で反応ガスの拡散速度が高まると共に、電極と反対側の固体高分子電解質膜側で水素イオンの導電速度が高まる。この結果、請求項1および請求項6記載の燃料電池によれば、電極触媒層における触媒の利用効率を高めて電極反応をより円滑で活発にし、電池性能をより一層向上することができる。

【0115】また、請求項2ないし請求項5および請求項7記載の燃料電池の製造方法によれば、準備した混合溶液の静置、或いは混合溶液への遠心作用、若しくは二以上の薄膜の積層等の簡便な工程を探るだけで、高い電池性能を有する燃料電池を製造することができる。

【0116】請求項3記載の燃料電池の製造方法によれば、その製造時間を短縮化することができる。

【0117】請求項4記載の燃料電池の製造方法によれ

ば、触媒担持体の積層自体でその底側ほど触媒担持体間の空隙を大きく底から離れるほど触媒担持体間の空隙を小さくできる。よって、電極触媒層においては、固体高分子電解質膜側でより水素イオンの導電性が高く電極側でより反応ガスの拡散透過性が高い燃料電池を製造することができる。

【01118】請求項6記載の燃料電池では、固体高分子電解質膜を必要としないので、燃料電池の構成ばかりか、その製造工程をも簡略化することができる。

【図面の簡単な説明】

【図1】実施例における燃料電池のセル構造の模式図。

【図2】第1実施例の製造工程を説明するためのものであり、触媒担持カーボンのペースト印刷物における沈降の初期の様子を模式的に表わした模式図。

【図3】同じく、触媒担持カーボンのペースト印刷物における沈降の様子を模式的に表わした模式図。

【図4】第1実施例のカソード側電極触媒層12における触媒担持カーボンと高分子電解質の存在の様子を模式的に表わした模式図。

【図5】第2実施例のカソード側電極触媒層12における触媒担持カーボンと高分子電解質の存在の様子を模式

的に表わした模式図。

【図6】電極触媒層形成用ペーストから薄膜を形成するために第4実施例で用いた薄膜形成装置20の概略構成図。

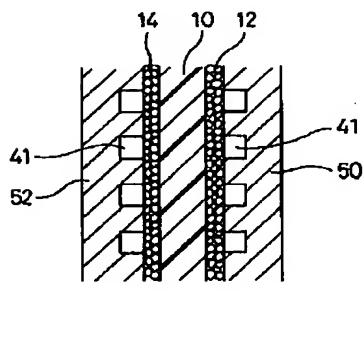
【図7】変形例における電極触媒層形成用ペーストを調製するために用いたペースト調製装置60の概略構成図。

【符号の説明】

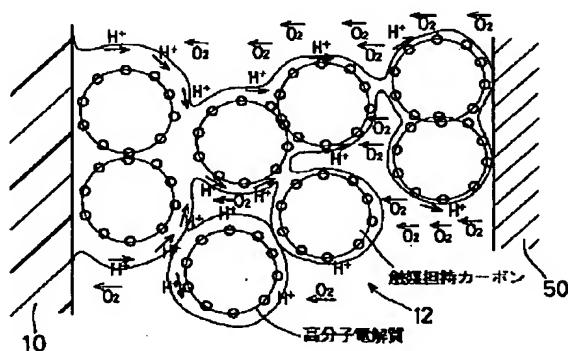
10…電解質膜

10	1 2…カソード側電極触媒層
	1 4…アノード側電極触媒層
	2 0…薄膜形成装置
	2 2…筒状回転容器
	2 4…ヒータ
	2 6…テフロンシート
	2 8…導入口
	3 0…吸引口
	3 2…電極触媒層形成用ペースト
20	4 1…流路
	5 0…カソード
	5 2…アノード

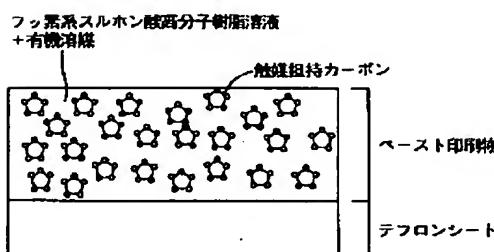
【図1】



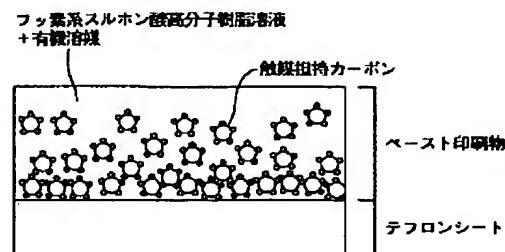
【図4】



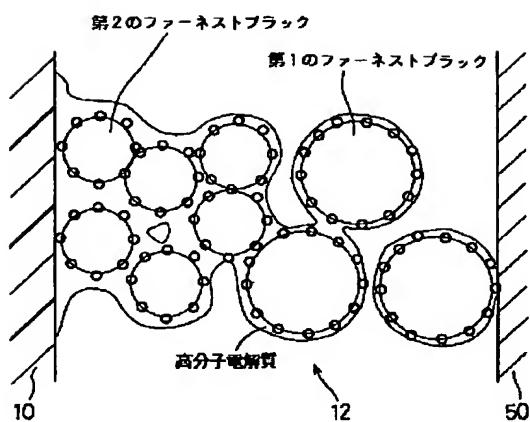
【図2】



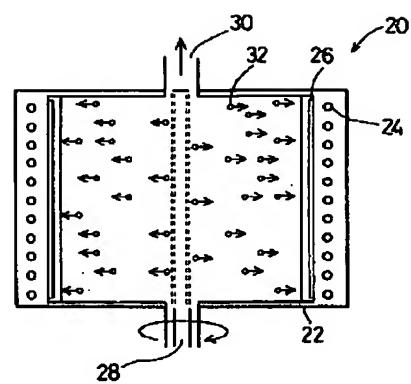
【図3】



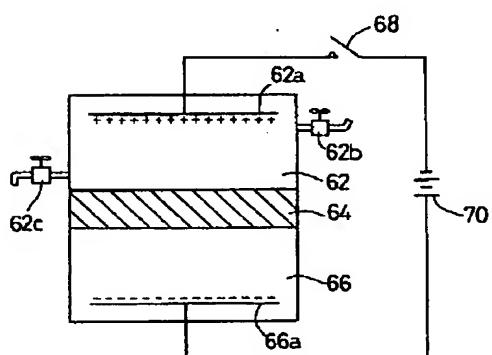
【図5】



【図6】



【図7】



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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the fuel cell which the electrode catalyst bed was made to be placed between the solid-state polyelectrolyte films which have the permselectivity of a hydrogen ion by catalyst \*\*\*\*, and was pinched with the electrode of the gaseous diffusion nature of a pair, and its manufacture method.

[0002]

[Description of the Prior Art] In this kind of fuel cell, electrode reaction shown by the reaction formula described below according to that polarity in the two electrodes which pinch a solid-state polyelectrolyte film was advanced, and electrical energy has been obtained.

[0003] Anode (hydrogen pole):  $H_2 \rightarrow 2H + 2e^-$  \*\* [0004] Cathode (oxygen pole):  $2H + 2e^- + (1/2) O_2 \rightarrow H_2O$  -- \*\* [0005] The reaction of formula \*\* is presented with the hydrogen ion which the hydrogen ion generated by the reaction of formula \*\* with the anode penetrated the solid-state polyelectrolyte film in the state of the hydration of  $H^+$  ( $xH_2O$ ) (diffusion), and penetrated the film with a cathode. The electrode reaction in this anode and cathode makes a reaction site the electrode catalyst bed stuck to the solid-state polyelectrolyte film, and advances by the interface of the catalyst and solid-state polyelectrolyte film in the electrode catalyst bed concerned.

[0006] If the interface of this catalyst and a solid-state polyelectrolyte film increases and interface formation equalizes, the reaction of above-mentioned \*\* and above-mentioned \*\* will advance more smoothly and actively. Therefore, in a Patent Publication table common 5-507583, the technology which makes an electrode catalyst bed the thing in the condition that catalyst support carbon was distributed by the proton conductivity ionomer is proposed in order to attain increase and equalization of this interface. In addition, a proton conductivity ionomer does not become the polyelectrolyte solution (Nafion solution: Nafion trade name of U.S. Du Pont) which demonstrates selection transparency of the hydrogen ion which is the same function as a solid-state polyelectrolyte film outside.

[0007] The paste for electrode catalyst bed formation with which catalyst support carbon was distributed by the polyelectrolyte solution is used for formation of this electrode catalyst bed. That is, the electrode catalyst bed which stuck the sheet which carried out film shaping, and which applied this paste for electrode catalyst bed formation to the solid-state polyelectrolyte film directly, or was obtained from the paste to the solid-state polyelectrolyte film by pressing in a solid-state polyelectrolyte film is formed. Thereby, since, as for the interface of the catalyst in an electrode catalyst bed, about a solid-state polyelectrolyte film and a polyelectrolyte are also formed, increase and equalization of an interface are attained.

[0008]

[Problem(s) to be Solved by the Invention] The diffuse transmission of reactant gas and electric conduction of a hydrogen ion are indispensable. [ in / besides equalization of the increase of the interface of a catalyst / in / in above-mentioned carrying out smoothly and the above-mentioned activity of \*\* and \*\* of a reaction / an electrode catalyst bed / or interface formation in an anode and a cathode /

an electrode catalyst bed] However, in the fuel cell proposed in the above-mentioned official report, since catalyst support carbon is distributed on the average by the polyelectrolyte in the electrode catalyst bed, the following troubles are pointed out.

[0009] At the electrode catalyst bed by which catalyst support carbon was distributed by the polyelectrolyte, it is placed between the gaps between adjoining catalyst support carbon by the polyelectrolyte, and catalyst support carbon exists in the condition that it was bound with this polyelectrolyte. For this reason, if the amount of the polyelectrolyte in an electrode catalyst bed is increased, the macromolecule electrolysis mass by which it is placed between the gaps between catalyst support carbon will increase. Therefore, the opening between the catalyst support carbon in an electrode catalyst bed becomes small, and the diffusional permeability of reactant gas falls. On the other hand, it increases, so that the amount of polyelectrolytes of conductivity of the hydrogen ion in an electrode catalyst bed increases. On the other hand, if the amount of polyelectrolytes is lessened, while the opening between catalyst support carbon will become large and the diffusional permeability of reactant gas will increase, the conductivity of a hydrogen ion becomes low. That is, the diffusional permeability of reactant gas and the conductivity of a hydrogen ion are properties of being contrary.

[0010] As catalyst support carbon was described above by the change in the amount of polyelectrolytes in the conventional fuel cell currently distributed on the average by the polyelectrolyte in the electrode catalyst bed, the diffusional permeability of reactant gas and the conductivity of a hydrogen ion change. For this reason, it is difficult to reconcile the diffusional permeability of suitable reactant gas, and the conductivity of a hydrogen ion in an electrode catalyst bed, and the room of improvement in the cell engine performance is left behind.

[0011] Moreover, about the diffusional permeability of reactant gas, a high thing is desirable outside the electrode catalyst bed inside (solid-state polyelectrolyte film side) (gas diffusion electrode side) on the necessity of carrying out diffuse transmission of the reactant gas promptly from the inflow part. On the other hand, about the conductivity of a hydrogen ion, it is desirable that it is higher than the convenience top which makes a solid-state polyelectrolyte film diffuse a hydrogen ion promptly, and a gas diffusion electrode side at a solid-state polyelectrolyte film side. However, in the above-mentioned conventional fuel cell, the diffusional permeability of reactant gas and the conductivity of a hydrogen ion continue outside from the inside of an electrode catalyst bed, and become respectively uniform. For this reason, height cannot be attached to the diffusional permeability of reactant gas, and the conductivity of a hydrogen ion on the inside and the outside of a layer, but the room of improvement in the cell engine performance is left behind also from this point. If it puts in another way, it will continue outside from the inside of a layer and the diffusion rate of the reactant gas by the side of a gas diffusion electrode will be restrained by the diffusional permeability of uniform reactant gas. On the other hand, the electric conduction speed of the hydrogen ion by the side of a solid-state polyelectrolyte film is restrained by the conductivity of an uniform hydrogen ion. For this reason, the effectiveness of the catalyst use in an electrode catalyst bed is low, and the further improvement in the cell engine performance was checked.

[0012] It aims at offering the simple manufacture method of a fuel cell of having the high cell engine performance while this invention is made in order to solve the above-mentioned trouble, and it aims at further improvement in the cell engine performance.

[0013]

[Means for Solving the Problem] A means which a fuel cell according to claim 1 adopted in order to attain this purpose An electrode catalyst bed which comes to carry out the laminating of the catalyst support is stuck on a solid-state polyelectrolyte film which has the permselectivity of a hydrogen ion. It is the fuel cell which this electrode catalyst bed was made to intervene and pinched this solid-state polyelectrolyte film with an electrode of the gaseous diffusion nature of a pair. Said electrode catalyst bed Come to carry out the laminating of the catalyst support covered with a polyelectrolyte which has the permselectivity of a hydrogen ion, and an opening between catalyst support in said electrode catalyst bed Let it be the summary to be made larger than said solid-state polyelectrolyte film side at said electrode side by changing said amount of polyelectrolytes which covers said catalyst support along the direction of a laminating of said catalyst support.

[0014] And a procedure adopted by manufacture method according to claim 2 in order to manufacture this fuel cell according to claim 1 A preparation production process for which a mixed solution of said catalyst support and said polyelectrolyte solution, and an volatile organic solvent is prepared, A standing production process which puts this mixed solution on environment where extend in the shape of a thin film, and said volatile organic solvent does not volatilize, gently [ time amount to which said catalyst support can sediment ], From a mixed solution extended in the shape of [ said ] a thin film, a film formation production process which forms a thin film through desiccation processing, and a this formed thin film so that a film surface of a side which had become the upper surface at the time of said standing may join to a film surface of said solid-state polyelectrolyte film Let it be the summary to have an adhesion production process stuck to said solid-state polyelectrolyte film.

[0015] Moreover, a procedure adopted by manufacture method according to claim 3 A preparation production process for which a mixed solution of said catalyst support and said polyelectrolyte solution, and an volatile organic solvent is prepared, A thin film-ized production process which puts this mixed solution into a tumbler which is put on environment where said volatile organic solvent does not volatilize, and rotates, exerts centrifugal force on this intrusion rare \*\*\*\*\*\*, and extends this mixed solution in the shape of a thin film, From a mixed solution extended in the shape of [ said ] a thin film, a film formation production process which forms a thin film through desiccation processing, and a this formed thin film so that a film surface of a side which had turned into the inside within a tumbler at the time of rotation of said tumbler may join to a film surface of said solid-state polyelectrolyte film Let it be the summary to have an adhesion production process stuck to said solid-state polyelectrolyte film.

[0016] In this case, by manufacture method of a fuel cell according to claim 4, it considered as a production process for which a mixed solution of at least two or more catalyst support from which particle size differs a preparation production process according to claim 2 or 3, said polyelectrolyte solution, and an volatile organic solvent is prepared.

[0017] Moreover, a procedure separately adopted by manufacture method according to claim 5 in order to manufacture a fuel cell according to claim 1 A production process for which said catalyst support and said polyelectrolyte solution, and an volatile organic solvent are mixed, and two or more mixed solutions with which said amounts of polyelectrolytes to said catalyst support differ are prepared, this using two or more mixed solutions with a production process which forms two or more thin films with which said amounts of polyelectrolytes to said catalyst support differ Let it be the summary to have a production process which carries out the laminating of the two or more formed this thin films to order with many said amounts of polyelectrolytes to said catalyst support at said solid-state polyelectrolyte film.

[0018] Moreover, a means which a fuel cell according to claim 6 adopted in order to attain the above-mentioned purpose An electrode catalyst bed which comes to carry out the laminating of the catalyst support, and an electrode of gaseous diffusion nature are stuck, and it is the fuel cell which it has a pair every. Said electrode catalyst bed Come to carry out the laminating of the catalyst support covered with a polyelectrolyte which has the permselectivity of a hydrogen ion, and an opening between catalyst support in said electrode catalyst bed By changing said amount of polyelectrolytes which covers said catalyst support along the direction of a laminating of said catalyst support, it is enlarged by said electrode side and an electrode catalyst bed of said pair makes it the summary to be joined so that sides with a small opening between said catalyst support may stick.

[0019] And a procedure adopted by manufacture method according to claim 7 in order to manufacture this fuel cell according to claim 6 A preparation production process according to claim 2 or 3 and a production process of either a standing production process according to claim 2 or a thin film-ized production process according to claim 3, A film formation production process according to claim 2 or 3 and a production process which carries out pair preparation of the this formed thin film, In a cementation production process which is made to stick the film surfaces of a side which had become the upper surface in said standing production process at the time of standing about a thin film of a prepared this pair, and is joined Let it be the summary to have one cementation production process of the cementation production processes which are made to stick the film surfaces of a side which had turned into the inside

within a tumbler in said thin film-ized production process in a thin film of a prepared this pair, and are joined.

[0020]

[Function] With the fuel cell according to claim 1 which has the above-mentioned configuration, the laminating of the catalyst support in an electrode catalyst bed is carried out in the condition of having been covered with the polyelectrolyte which has the permselectivity of a hydrogen ion. between adjoining catalyst support, contact of the polyelectrolytes of the circumference of catalyst support cuts. By the way, since the amount of polyelectrolytes is changed along the direction of a laminating of catalyst support, contact of the polyelectrolytes of the circumference of catalyst support will set, and condition will also change along the direction of a laminating of catalyst support. It is reflected in the amount of polyelectrolytes which occupies the gap between the catalyst support which condition adjoins by on the other hand contact of the polyelectrolytes of the circumference of catalyst support setting. Therefore, the amount of polyelectrolytes which occupies the gap between the catalyst support which adjoins if there are many amounts of polyelectrolytes also increases, the opening between catalyst support becomes small, if there are few amounts of polyelectrolytes, the amount of polyelectrolytes which occupies a gap will also decrease and the opening between catalyst support will become large. For this reason, in a fuel cell according to claim 1, the opening between the catalyst support in an electrode catalyst bed is enlarged by the electrode side from a solid-state polyelectrolyte film side by changing the amount of polyelectrolytes, and the diffusional permeability of reactant gas can be raised by the electrode side, and can be made low by the solid-state polyelectrolyte film side. On the other hand, about the amount of polyelectrolytes, with the opening between catalyst support, it can increase more than an electrode side conversely in a solid-state polyelectrolyte film side, the conductivity of a hydrogen ion can be raised to it by the solid-state polyelectrolyte film side, and it can be made low by the electrode side.

[0021] By the manufacture method according to claim 2, catalyst support is made into the condition of having been covered with the polyelectrolyte solution, through distribution of the catalyst support in the inside of a mixed solution by passing through a preparation production process. Then, catalyst support is made to sediment by passing through a standing production process in the mixed solution extended in the shape of a film. By this sedimentation, the laminating of the catalyst support is carried out to the bottom side of the mixed solution extended in the shape of a film. On the other hand, although a polyelectrolyte solution exists where catalyst support is covered in the laminating of catalyst support, it exists also as a supernatant of a laminating with an organic solvent.

[0022] Subsequently, catalyst support forms the thin film which comes to carry out a laminating by passing through a film formation production process. That is, desiccation evaporation of the part for the volatile organic solvent in a mixed solution and the solution of a polyelectrolyte solution is carried out between processings of desiccation of a film formation production process. Thereby, while each catalyst support covered with the polyelectrolyte solution is covered with a polyelectrolyte, the thin film this catalyst support carried out [ the thin film ] the laminating is formed. In this case, since a polyelectrolyte solution is made to exist as a supernatant of the laminating of catalyst support in a standing production process, the upper catalyst support in a laminating is further covered with the polyelectrolyte of the polyelectrolyte solution in this supernatant. That is, in the side which had become the upper surface at the time of the upper part of the laminating of catalyst support, i.e., standing, the amount of polyelectrolytes which covers catalyst support increases. Therefore, in the thin film in which catalyst support comes to carry out a laminating, in the base side, there are few amounts of polyelectrolytes and the amount of polyelectrolytes increases by the upper surface side of a thin film. For this reason, by the upper surface side (side which had become the upper surface at the time of standing) with many amounts of polyelectrolytes, the opening between small catalyst support and the conductivity of a high hydrogen ion are discovered, and the conductivity of the opening between the large catalyst support at a base side with few amounts of polyelectrolytes and a low hydrogen ion is discovered with this thin film.

[0023] Then, when it passes through an adhesion production process, the thin film upper surface which the conductivity of a hydrogen ion small the opening between catalyst support and high discovered will

join to the film surface of a solid-state polyelectrolyte film. The thin film base which the opening between catalyst support low the conductivity of a hydrogen ion and big on the other hand discovered will become the electrode side of gaseous diffusion nature, if a fuel cell is completed through pinching with the electrode of the gaseous diffusion nature of a pair.

[0024] By the manufacture method according to claim 3, catalyst support is made into the condition of having been covered with the polyelectrolyte solution, by passing through a preparation production process. Then, by passing through a thin film-sized production process, in a tumbler, centrifugal force is exerted on a mixed solution, and this mixed solution is extended in the shape of a film in accordance with a container wall. And catalyst support is made to sediment compulsorily according to centrifugal force in the mixed solution extended in the shape of a film. By this sedimentation, the laminating of the catalyst support is carried out to the bottom side (container wall side) of the mixed solution extended in the shape of a film in the inside of a short time. On the other hand, although a polyelectrolyte solution exists where catalyst support is covered in the laminating of catalyst support, it exists also as a supernatant of a laminating with an organic solvent.

[0025] Subsequently, catalyst support forms the thin film which comes to carry out a laminating like the manufacture method according to claim 2 by passing through a film formation production process. That is, the catalyst support covered by the desiccation evaporation for a solution of the organic solvent between processings of desiccation of a film formation production process or a polyelectrolyte solution by the polyelectrolyte forms the thin film which comes to carry out a laminating. In this case, in a thin film-sized production process, like a standing production process according to claim 2, since a polyelectrolyte solution is made to exist as a supernatant of the laminating of catalyst support, the amount of polyelectrolytes which covers catalyst support is made [many] in the upper part of the laminating of catalyst support, i.e., the inside within a tumbler. Therefore, in the thin film in which catalyst support comes to carry out a laminating, there are few amounts of polyelectrolytes and the amount of polyelectrolytes increases in an upper surface side at the base side. For this reason, by the upper surface side (inside within a tumbler) with many amounts of polyelectrolytes, the opening between small catalyst support and the conductivity of a high hydrogen ion are discovered, and the conductivity of the opening between the large catalyst support at a base side with few amounts of polyelectrolytes and a low hydrogen ion is discovered with this thin film as well as the manufacture method according to claim 2.

[0026] Then, when it passes through an adhesion production process, the thin film upper surface which the conductivity of a hydrogen ion small the opening between catalyst support and high discovered will join to the film surface of a solid-state polyelectrolyte film. The thin film base which the opening between catalyst support low the conductivity of a hydrogen ion and big on the other hand discovered becomes the electrode side of gaseous diffusion nature.

[0027] By the manufacture method of a fuel cell according to claim 4, we decided to prepare the mixed solution which mixed at least two or more catalyst support from which particle size differs in the preparation production process according to claim 2 or 3. Therefore, in the mixed solution extended in the shape of a film, catalyst support with a large particle size sediments previously, and it sediments so late that particle size is small. For this reason, the laminating of catalyst support serves as a pile of the laminating section according to the particle size of catalyst support. And in each laminating section, the openings between adjoining catalyst support differ the whole laminating section from the particle size of catalyst support differing. That is, the laminating section in which this rate is large and the laminating section by the side of the bottom of a mixed solution separates from a bottom side becomes small.

[0028] Therefore, by passing through a subsequent production process, by the electrode catalyst bed, the opening between catalyst support is small at the side joined to a solid-state polyelectrolyte film, the conductivity of a hydrogen ion becomes high, the conductivity of a hydrogen ion is more low at the electrode side of gaseous diffusion nature, and the opening between catalyst support becomes large.

[0029] By the manufacture method according to claim 5, two or more mixed solutions with which the amounts of polyelectrolytes to catalyst support differ are prepared, and two or more thin films with which these amounts of polyelectrolytes differ are formed. And the laminating of the two or more thin

films is carried out to a solid-state polyelectrolyte film at order with many amounts of polyelectrolytes. Therefore, since the amount of polyelectrolytes increases as a solid-state polyelectrolyte film side, also by this manufacture method, in an electrode catalyst bed, the opening between catalyst support is small at a solid-state polyelectrolyte film side, the conductivity of a hydrogen ion becomes high, the conductivity of a hydrogen ion is more low at the electrode side of gaseous diffusion nature, and the opening between catalyst support becomes large.

[0030] Moreover, even if it is in a fuel cell according to claim 6, by changing the amount of polyelectrolytes along the direction of a laminating of catalyst support, like the fuel cell according to claim 1, the opening between the catalyst support in an electrode catalyst bed is enlarged by the electrode side, and diffusional permeability of reactant gas is made it is high and low by the electrode side in the opposite side. On the other hand, about the amount of polyelectrolytes, with the opening between catalyst support, it becomes it is small and large by the electrode side in the opposite side at reverse, and conductivity of a hydrogen ion can be made it is low and high by the electrode side in the opposite side. And the electrode catalyst bed of a pair is joined so that sides with the small opening between catalyst support, i.e., sides with the conductivity of a hydrogen ion there are many amounts of polyelectrolytes and high, may stick. Therefore, the adhesion field of sides where there are many these amounts of polyelectrolytes and the conductivity of a hydrogen ion is high functions in a fuel cell as an electrolyte film which has the permselectivity of a hydrogen ion.

[0031] By the manufacture method according to claim 7, catalyst support is made into the condition of having been covered with the polyelectrolyte solution, by passing through a preparation production process. It is passing through the production process of either a standing production process or a thin film-sized production process after that, sedimentation of catalyst support is aimed at in the mixed solution extended in the shape of a film, and the laminating of the catalyst support is carried out to the bottom side of the mixed solution extended in the shape of a film. On the other hand, a polyelectrolyte solution is made to exist, where catalyst support is covered in the laminating of catalyst support, and is made to exist also as a supernatant with an organic solvent on a laminating.

[0032] Subsequently, the catalyst support covered with passing through a film formation production process with the polyelectrolyte by the desiccation evaporation for a solution of an organic solvent or a polyelectrolyte solution forms the thin film which comes to carry out a laminating. In this case, since a polyelectrolyte solution is made to exist as a supernatant of the laminating of catalyst support in a before production process, in the upper part of the laminating of catalyst support, the amount of polyelectrolytes which covers catalyst support is made [ many ]. Therefore, in the thin film in which catalyst support comes to carry out a laminating, there are few amounts of polyelectrolytes and the amount of polyelectrolytes increases in an upper surface side at the base side. For this reason, by the upper surface side with many amounts of polyelectrolytes, the opening between small catalyst support and the conductivity of a high hydrogen ion are discovered, and the conductivity of the opening between the large catalyst support at a base side with few amounts of polyelectrolytes and a low hydrogen ion is discovered with this thin film.

[0033] Then, if it passes through one of cementation production processes, sides with the conductivity of a hydrogen ion there are many amounts of polyelectrolytes and high will stick, and the adhesion field will turn into a field which achieves the same function as the solid-state polyelectrolyte film which has the permselectivity of a hydrogen ion in a fuel cell. Moreover, the conductivity of a hydrogen ion has an opening between low and big catalyst support, and the side and the opposite side where there are many amounts of polyelectrolytes and the conductivity of a hydrogen ion is high stick it the electrode side of gaseous diffusion nature.

[0034] [Example] Next, in order to clarify a configuration and an operation of this invention further, the suitable example of this invention is explained below. Drawing 1 is the mimetic diagram of the cellular structure of the fuel cell (polymer electrolyte fuel cell) in this example.

[0035] The cel is constituted by the electrolyte film 10 which is a film-like electrolyte, the cathode lateral electrode catalyst bed 12 and the anode lateral electrode catalyst bed 14 stuck to the film surface

of this electrolyte film 10, and the cathode 50 and anode 52 which were stuck to each [ these ] electrode catalyst bed so that it may illustrate.

[0036] The electrolyte film 10 is a solid-state polyelectrolyte film to a hydrogen ion which has a sulfone radical as an ion exchange group, and penetrates a hydrogen ion alternatively along the direction of thickness. When it explains concretely, the electrolyte film 10 is a solid-state polyelectrolyte film (for example, perfluorocarbon-sulfonic-acid poly membrane (trade name: Nafion and product made from Du Pont)) produced from fluorine system sulfonic-acid macromolecule resin, and the thickness is about 120 micrometers.

[0037] The cathode lateral electrode catalyst bed 12 and the anode lateral electrode catalyst bed 14 intervene between a cathode 50, an anode 52, and the electrolyte film 10, and they are passing through these hotpresses and it is stuck to them in the film surface of the electrolyte film 10, and the electrode surface by the side of the electrolyte of each electrode. this cathode lateral electrode catalyst bed 12 and the anode lateral electrode catalyst bed 14 -- as a catalyst -- platinum -- 20wt(s)% -- the supported carbon particle should carry out a laminating and pass the below-mentioned manufacturing process -- it is formed. In addition, in drawing 1, the carbon particle which constitutes the cathode lateral electrode catalyst bed 12 and the anode lateral electrode catalyst bed 14 is exaggerated and drawn.

[0038] A cathode 50 and an anode 52 are formed with conductive porous carbon while they have gas permeability by porosity, and the porosity is 60 thru/or 80%. Moreover, passage 41 is formed in the electrode catalyst bed side corresponding to a cathode 50 and an anode 52, respectively. In addition, this cathode 50 and anode 52 also achieve the function as a separator to divide the adjoining fuel cell cel from it being porous carbon.

[0039] The fuel gas with which the fuel cell of a configuration of having described above was supplied when fuel gas (humidification hydrogen gas, oxygen gas) was supplied to each pole from passage 41 and 43 penetrates a cathode 50 and an anode 52 (diffusion), and results in the cathode lateral electrode catalyst bed 12 and the anode lateral electrode catalyst bed 14. And in the electrode catalyst bed concerned, the reaction shown in formula \*\* mentioned above and \*\* is presented with the fuel gas. That is, in an anode 52 side, the reaction of formula \*\* is presented with the hydrogen ion which the hydrogen ion generated by advance of the reaction of formula \*\* penetrated the electrolyte film 10 in the state of the hydration of  $H^+ (xH_2O)$  (diffusion), and penetrated the film with a cathode 50. In addition, this reaction is promoted by the catalysis of the cathode lateral electrode catalyst bed 12 and the anode lateral electrode catalyst bed 14, and advances.

[0040] Next, order is explained later on about the manufacturing process of the above-mentioned fuel cell (cel). The preparation production process which prepares the mixed solution of catalyst support carbon, a polyelectrolyte solution, and an volatile organic solvent for the beginning is explained. At this preparation production process, weighing capacity of the mixed object is carried out as follows first. that is, platinum (mean particle diameter of about 1nm) -- 20wt(s)% -- 10ml weighing capacity of the fluorine system sulfonic-acid macromolecule resin solution (solution with which the solid content of the resin concerned was blended at 5wt(s)% ) homogeneous as the electrolyte film 10 is carried out to supported catalyst support carbon (mean particle diameter of about 20nm) 1g. Furthermore, weighing capacity of ethylene glycol mono-isopropyl ether and every 5ml of the isopropanols is carried out as an organic solvent, respectively. In addition, not only an organic solvent but other than the aforementioned solvent, distribution of carbon is good and should not just have a bad influence on an electrolyte film.

[0041] And the catalyst support carbon, fluorine system sulfonic-acid macromolecule resin solution, and organic solvent of only a required amount are prepared by this ratio. Subsequently, the prepared catalyst support carbon is put into a well-closed container, and ultrasonic distribution of the catalyst support carbon is carried out in this well-closed container. In this way, the mixed solution for a preparation production process being completed and forming an electrode catalyst bed, i.e., the paste for electrode catalyst bed formation, is prepared. In this preparation production process, catalyst support carbon will be in the condition of it having been covered with the fluorine system sulfonic-acid macromolecule resin solution, and having distributed in the solution.

[0042] In this case, various the amounts of solutions of the fluorine system sulfonic-acid macromolecule

resin solution to catalyst support carbon 1g can be changed. However, it is required to be the capacity which each catalyst support carbon can cover with the fluorine system sulfonic-acid macromolecule resin in a fluorine system sulfonic-acid macromolecule resin solution.

[0043] It is desirable to cool beforehand a well-closed container besides raw materials, such as prepared catalyst support carbon, on the occasion of this preparation production process. Thus, it is because it can prevent that an organic solvent steam and the oxygen in air react according to a platinum catalyst if it cools. Moreover, or inert gas replaces a well-closed container, the treatment under thin oxygen is also effective at the point of preventing the reaction of an organic solvent steam. Furthermore, water, a ketone, ester, etc. can add oxygen and the solvent which does not react to the degree which does not have a bad influence on the rheology property of the paste for electrode catalyst bed formation, and can also be mixed to it. In addition, it can change to ultrasonic distribution and the distributed method using a homogenizer, a ball mill, a planetary mill, etc. can also be taken.

[0044] After that, the following standing production processes are performed. That is, a Teflon sheet with a thickness of 300 micrometers is first fixed to the upper surface of the plate maintained horizontally as front preparation, and the Teflon sheet surface is washed by ethanol. Subsequently, the paste for electrode catalyst bed formation of finishing [ the above-mentioned preparation ] is dropped at the Teflon sheet surface, the paste for electrode catalyst bed formation is delayed in the shape of a thin film by the homogeneity thickness of 200 micrometers with a doctor blade, and paste printed matter is obtained. Under the present circumstances, the electrode catalyst bed of the various thickness of catalysts, i.e., the various amounts, can be obtained by adjusting the path clearance of a doctor blade.

[0045] Next, the paste printed matter on a Teflon sheet is laid in a well-closed container, and is put for 24 hours. If it continues between this standing, the same organic solvent as the organic solvent of the paste for electrode catalyst bed formation is enclosed with that maximum vapor tension in the well-closed container. Therefore, standing of the paste printed matter will be carried out under the environment where the organic solvent of a paste does not volatilize. Between this standing, the catalyst support carbon in the paste for electrode catalyst bed formation sediments in paste printed matter. The situation of this sedimentation is typically expressed to drawing 2 and drawing 3.

[0046] That is, the catalyst support carbon which was being distributed in paste printed matter as shown before standing at drawing 2 sediments between standing, and as shown in drawing 3, it carries out a laminating to the bottom side of paste printed matter. In this case, roughness and fineness extreme in the laminating condition of catalyst support carbon are not seen, but the laminating of the catalyst support carbon is mostly distributed and carried out to homogeneity. On the other hand, although a fluorine system sulfonic-acid macromolecule resin solution exists where catalyst support carbon is covered in the laminating of catalyst support carbon, it exists also as a supernatant of a laminating with an organic solvent. In addition, the settling time of 24 hours is sufficient time amount for catalyst support carbon to sediment in paste printed matter.

[0047] Subsequently, after giving paste printed matter to ordinary temperature desiccation, it carries out on a vacuum drying at 50 degrees C, and a film formation production process is performed. That is, the amount of [ an organic solvent and / of a fluorine system sulfonic-acid macromolecule resin solution ] solution carries out desiccation evaporation, and they are removed from paste printed matter by this vacuum drying. For this reason, while each catalyst support carbon covered with the fluorine system sulfonic-acid macromolecule resin solution by passing through this film formation production process is covered with the fluorine system sulfonic-acid macromolecule resin which is a polyelectrolyte, the thin film this catalyst support carbon carried out [ the thin film ] the laminating is formed. In this case, since a fluorine system sulfonic-acid macromolecule resin solution exists as a supernatant of the laminating of catalyst support carbon in a standing production process, the upper catalyst support carbon in a laminating is further covered with the fluorine system sulfonic-acid macromolecule resin of the fluorine system sulfonic-acid macromolecule resin solution in this supernatant. In addition, if it is in the following explanation, fluorine system sulfonic-acid macromolecule resin is only called polyelectrolyte.

[0048] That is, in the side which had become the upper surface at the time of the upper part of the laminating of catalyst support carbon, i.e., standing, the amount of polyelectrolytes which covers

catalyst support carbon increases. Therefore, in the formed thin film, in the base side, there are few amounts of polyelectrolytes and the amount of polyelectrolytes increases by the upper surface side of a thin film. For this reason, this thin film is equipped with the opening between small catalyst support carbon, and the conductivity of a high hydrogen ion by the film upper surface side with many amounts of polyelectrolytes. On the other hand, the amount of polyelectrolytes will be equipped with the opening between large catalyst support carbon, and the conductivity of a low hydrogen ion by few bases side. [0049] After that, the fuel cell (cel) was completed as follows. First, the hotpress (126 degree-Cx100 kg/cm<sup>2</sup>) of the paste printed matter after a vacuum drying is carried out to both the film surfaces of the electrolyte film 10 in piles the whole Teflon sheet, and a Teflon sheet is removed after this hotpress. Subsequently, where this electrolyte film 10 is pinched with a cathode 50 and an anode 52, the hotpress (126 degree-Cx100 kg/cm<sup>2</sup>) was carried out further. While the cathode lateral electrode catalyst bed 12 and the anode lateral electrode catalyst bed 14 are formed from the paste for electrode catalyst bed formation through each above-mentioned production process, the fuel cell (cel) which has a two-electrodes catalyst bed is completed. In addition, a Teflon sheet may be removed in advance of a hotpress; paste printed matter may be put on both the film surfaces of the electrolyte film 10, and a hotpress may be carried out where the both sides are further pinched with a cathode 50 and an anode 52. [0050] In this way, the cathode lateral electrode catalyst bed 12 is taken for an example, and the situation of the existence of the catalyst support carbon in the cathode lateral electrode catalyst bed 12 and the anode lateral electrode catalyst bed 14 which were formed, and a polyelectrolyte is explained with drawing.

[0051] As the cathode lateral electrode catalyst bed 12 is shown in drawing 4 expressed typically, each catalyst support carbon is covered with the polyelectrolyte. However, there are many amounts [ few ] of polyelectrolyte covering at the electrolyte film 10 side per, catalyst support carbon at a cathode 50 side. There are many amounts [ few ] of mediation at the electrolyte film 10 side to which it is placed between the gaps between the catalyst support carbon which adjoins on the other hand by the polyelectrolyte at a cathode 50 side. For this reason, the opening between the catalyst support carbon as an electrode catalyst bed is [ in a cathode 50 side ] greatly small at the electrolyte film 10 side. Therefore, diffusion of the hydrogen ion from the film surface of the electrolyte film 10 to the cathode lateral electrode catalyst bed 12 is promptly performed from there being many amounts of polyelectrolytes by the electrolyte film 10 side of the cathode lateral electrode catalyst bed 12. And diffuse transmission of the reactant gas (oxygen gas) from the cathode 50 to the cathode lateral electrode catalyst bed 12 is promptly performed from the opening between catalyst support carbon being large by the cathode 50 side of the cathode lateral electrode catalyst bed 12.

[0052] For this reason, according to the cathode lateral electrode catalyst bed 12 and the anode lateral electrode catalyst bed 14, the conductivity of the hydrogen ion to the electrolyte film 10 can be raised from the electrolyte film 10. On the other hand, in a cathode 50 and anode 52 side, the diffusional permeability of the reactant gas from these electrodes can be raised.

[0053] Therefore, in the fuel cell of this example, in an electrode catalyst bed, the diffusion rate of reactant gas can be raised by the cathode 50 and anode 52 side, and the electrolyte film 10 side can raise the electric conduction speed of a hydrogen ion. Consequently, according to the fuel cell of this example, the use effectiveness of the catalyst in an electrode catalyst bed can be raised, electrode reaction can be made more smoothly and active, and the cell engine performance can be improved further.

[0054] Next, the performance evaluation of the fuel cell of this example (the 1st example) which has the above-mentioned cathode lateral electrode catalyst bed 12 and the anode lateral electrode catalyst bed 14 is explained. Although the example fuel cell of a comparison (conventional article) to contrast was equipped with the same cell configuration as the above-mentioned example, it skipped the standing production process and performed formation of the electrode catalyst bed by the side of a cathode and an anode. That is, in the example fuel cell of a comparison, paste printed matter was produced by the homogeneity thickness of 200 micrometers with the doctor blade from the same paste for electrode catalyst bed formation as the 1st example, the thin film was carried out immediately, and the hotpress

was carried out to the electrolyte film 10. And the I-V property was investigated about both fuel cells. The result is shown in a table 1. In addition, the evaluation conditions are as follows. Moreover, the property of the fuel cell in the 2nd thru/or the 6th example mentioned later is also put on this table 1.

[0055] Electrode area: 144cm<sup>2</sup>; (12cmx12cm)

Cel temperature: 75 degrees C;

reagent-gas-pressure: -- anode; -- hydrogen 0.2MPa (2ata) and cathode; air 0.2MPa(2ata);

The gas humidification method: The bubbling method (anode water temperature of 90 degrees C,

cathode water temperature of 80 degrees C);

rate of gas utilization: -- anode; -- 50% and cathode;20%;

[0056]

[A table 1]

	サンプル区分	電流密度 (mA/cm <sup>2</sup> )			
		300	500	1000	1500
電 圧	比較例	1	0. 80	0. 69	放電不能
	第1実施例	1. 04	0. 94	0. 72	0. 48
	第2実施例	1. 05	0. 95	0. 76	0. 52
	第3実施例	1. 04	0. 95	0. 77	0. 58
	第4実施例	1. 04	0. 94	0. 73	0. 49
	第5実施例	1. 05	0. 96	0. 79	0. 62
	第6実施例	1. 04	0. 94	0. 78	0. 50

[0057] For the numeric value (data) in this table 1, current density is 300 mA/cm<sup>2</sup> about the example fuel cell of a comparison. The cell voltage value measured at the case was set to 1, and it displayed about other fuel cells by the relative value which standardized that measured value with this cell voltage value.

[0058] In the fuel cell of the 1st example, the cell voltage higher than the example fuel cell of a comparison about each current density was obtained so that clearly from this table 1. in especially high current density (1500 mA/cm<sup>2</sup>), discharge is impossible with the example fuel cell of a comparison, and cannot be used -- receiving -- the fuel cell of the 1st example -- 300 mA/cm<sup>2</sup> the case of current density -- almost -- one half -- it is -- although -- cell voltage -- obtaining -- having had . Therefore, even if it is a high current density field in the fuel cell of the 1st example, the use effectiveness of the catalyst in an electrode catalyst bed can be maintained, and it is desirable.

[0059] Moreover, according to the manufacturing process of this example, the fuel cell which has the high cell engine performance can be manufactured only by taking the simple production process of putting paste printed matter.

[0060] Next, sequential explanation is given about other examples (the 2nd thru/or the 6th example).

[0061] It is different from the 1st example which described above the catalyst support carbon in the mixed solution (paste for electrode catalyst bed formation) prepared at the preparation production process with the point made into the following in the 2nd example, and the fuel cell cellular structure etc. is the same as the 1st example.

[0062] In this 2nd example, it sets at a preparation production process. The mixed furnace black which blended the 2nd supported furnace black (mean particle diameter of about 40nm) by the ratio of 1:1 is prepared. platinum with a mean particle diameter of about 1nm -- 20wt(s)% -- the 1st furnace black (mean particle diameter of about 20nm) and the platinum with a mean particle diameter of about 2nm which were supported -- 20wt(s)% -- With the same fluorine system sulfonic-acid macromolecule resin solution and same organic solvent as the 1st example, the paste for electrode catalyst bed formation was prepared. In this case, the amount of weighing capacity of a fluorine system sulfonic-acid macromolecule resin solution and each organic solvent to mixed furnace black 1g is the same as that of

the 1st example. that is, in this 2nd example, prepare the paste for electrode catalyst bed formation which the catalyst support (the 1st and 2nd furnace black) which is two kinds from which particle size differs distributed, and pass the same production processes (a standing production process, film formation production process, etc.) as the 1st example after that -- the fuel cell was manufactured.

[0063] In this case, at the standing production process of the 2nd example, in the paste printed matter obtained with the paste for electrode catalyst bed formation, the 2nd furnace black with a large particle size sediments previously, and the 1st furnace black with a small particle size sediments late. For this reason, the laminating section of the 2nd furnace black turns on the base side of paste printed matter, and the laminating section of the 1st furnace black is piled up on it. And in each laminating section, by the laminating section of the 2nd furnace black, the opening of the furnace black which adjoins from the particle size of furnace black differing is large, and becomes [ the laminating section of the 1st furnace black ] small.

[0064] And a fluorine system sulfonic-acid macromolecule resin solution exists as a supernatant of the laminating of furnace black also in this 2nd example. For this reason, the amount of polyelectrolytes which covers furnace black with the laminating section side of the 1st furnace black increases, and the amount of polyelectrolytes decreases in the laminating section side of the 2nd furnace black by the side of a base. And by passing through a subsequent production process, the laminating section of the 1st furnace black by the side of the upper surface of paste printed matter sticks to the electrolyte film 10, and it sticks to the electrode with which the laminating section of the 2nd furnace black by the side of a base corresponds. Therefore, the situation of the existence of the 1st and 2nd furnace black in the electrode catalyst bed formed in this 2nd example and a polyelectrolyte is as follows.

[0065] That is, as shown in drawing 5 which takes the cathode lateral electrode catalyst bed 12 for an example, and shows it typically, the 1st and 2nd furnace black is covered with the polyelectrolyte. However, there are many amounts [ few ] of polyelectrolyte covering at the electrolyte film 10 side per furnace black at a cathode 50 side. Since many amounts of mediation to which it is placed between the gaps between the adjoining furnace black by the polyelectrolyte on the other hand decrease by the cathode 50 side in the electrolyte film 10 side, they are [ in a cathode 50 side ] greatly small at the electrolyte film 10 side. [ of the opening between the catalyst support carbon as an electrode catalyst bed ] Therefore, diffusion of the hydrogen ion from the film surface of the electrolyte film 10 to the cathode lateral electrode catalyst bed 12 is promptly performed from there being many amounts of polyelectrolytes by the electrolyte film 10 side of the cathode lateral electrode catalyst bed 12. And diffuse transmission of the reactant gas (oxygen gas) from the cathode 50 to the cathode lateral electrode catalyst bed 12 is promptly performed from the opening between catalyst support carbon being large by the cathode 50 side of the cathode lateral electrode catalyst bed 12.

[0066] For this reason, also by the cathode lateral electrode catalyst bed 12 in the fuel cell of the 2nd example, and the anode lateral electrode catalyst bed 14, the diffusion rate of reactant gas can be raised by the cathode 50 and anode 52 side, and the electric conduction speed of a hydrogen ion can be raised by the electrolyte film 10 side. Consequently, also with the fuel cell of this 2nd example, the use effectiveness of the catalyst in an electrode catalyst bed can be raised, electrode reaction can be made more smoothly and active, and the cell engine performance can be improved further.

[0067] And while the cell voltage higher than the example fuel cell of a comparison about each current density was obtained also by the fuel cell of the 2nd example so that clearly from the data about the fuel cell of the 2nd example in a table 1, even if it was a high current density field, the use effectiveness of the catalyst in an electrode catalyst bed was maintainable.

[0068] Moreover, in this 2nd example, although the magnitude of the opening between catalyst support carbon particles is changed also by changing the particle size of catalyst support carbon, the particle of catalyst support carbon itself is distributed over abbreviation homogeneity. For this reason, as compared with the 1st above-mentioned example, the voltage drop in a high current density field can be made small.

[0069] Next, the 3rd example is explained. In this 3rd example, the class of catalyst support used for the paste for electrode catalyst bed formation is different from the 2nd above-mentioned example, and the

fuel cell cellular structure etc. is already the same as the 1st example of a beam.

[0070] In this 3rd example, furnace black and acetylene black were used in the preparation production process. and platinum with a mean particle diameter of about 1nm -- 20wt(s)% -- the furnace black (mean particle diameter of about 20nm) and the platinum with a mean particle diameter of about 3nm which were supported -- 20wt(s)% -- the supported acetylene black (mean particle diameter of about 40nm) was blended by the ratio of 1:1, and the paste for electrode catalyst bed formation was prepared.

[0071] Also in the standing production process of this 3rd example, acetylene black with a large particle size sediments previously, and the furnace black with a small particle size sediments late. For this reason, the laminating section of acetylene black turns on the base side of paste printed matter, and the laminating section of furnace black is piled up on it. And the laminating section of the furnace black by the side of the upper surface of paste printed matter sticks to the electrolyte film 10, and it sticks to the electrode with which the laminating section of the acetylene black by the side of a base corresponds.

Therefore, like the 2nd example, by the electrolyte film side of an electrode catalyst bed, there are many amounts of polyelectrolytes, the opening between catalyst support carbon is small, there are few amounts of polyelectrolytes at an electrode side, and the opening between catalyst support carbon becomes large. Therefore, also with the fuel cell of the 3rd example, the use effectiveness of the catalyst in an electrode catalyst bed can be raised, electrode reaction can be made more smoothly and active, and the cell engine performance can be improved further.

[0072] Moreover, while the cell voltage higher than the example fuel cell of a comparison about each current density was obtained also by the fuel cell of the 3rd example so that clearly from the data about the fuel cell of the 3rd example in a table 1, even if it was a high current density field, the use effectiveness of the catalyst in an electrode catalyst bed was maintainable.

[0073] In this 3rd example, acetylene black was used for the side stuck to the electrode (a cathode 50, anode 52) of an electrode catalyst bed as catalyst support. This acetylene black has hydrophobicity with them. [there are few surface functional groups and big] Therefore, the fuel cell of the 3rd example can give hydrophobicity to the cathode lateral electrode catalyst bed 12 and the anode lateral electrode catalyst bed 14 by the electrode side. For this reason, there are the following advantages.

[0074] When hydrophilicity with the strong carbon surface is shown, there is orientation for water to tend to collect between a polyelectrolyte and the carbon surface. Although there is an effect in raising raising and conductivity about the water content of a polyelectrolyte, superfluous moisture and when there is specifically superfluous generation water, this is made as for the phase of water to an interface with a polyelectrolyte, and checks the gaseous diffusion to a catalyst. On the contrary, when the carbon surface shows hydrophobicity, in an interface with a polyelectrolyte, water becomes is hard to be held and it is easy to obtain improvement in gaseous diffusion nature. For this reason, in the 3rd example, the flooding in an electrode catalyst bed can be controlled and descent of the output voltage in a high current density field can be further made small as compared with the 2nd example.

[0075] Next, the 4th example is explained. It changes to the standing production process in the 1st example, and is different from the 1st example with this 4th example at the point which took the thin film-sized production process of explaining below, and the presentation of the paste for electrode catalyst bed formation in the fuel cell cellular structure etc. and a preparation production process is the same as that of the 1st example.

[0076] At the thin film-sized production process adopted in this 4th example, a thin film is formed using a thin film deposition system from the paste for electrode catalyst bed formation prepared at the preparation production process in the 1st example. Here, in advance of explanation of a thin film-sized production process, the thin film deposition system 20 used for the production process concerned is explained.

[0077] As a thin film deposition system 20 is shown in drawing 6 showing the outline configuration, it has the tubed tumbler 22 in the air which rotates focusing on a medial axis, and the heater 24 which heats the inside of the tubed tumbler 22 is laid under the side wall. Moreover, the Teflon sheet 26 with a thickness of 300 micrometers is being fixed to the inner circle wall of the tubed tumbler 22 along with the peripheral wall. This Teflon sheet 26 can be freely removed to the inner circle wall of the tubed

tumbler 22, and that surface is washed by ethanol before attachment. Moreover, the organic solvent steam and the inlet 28 of the paste for electrode catalyst bed formation are formed in the center of a lower limit of the tubed tumbler 22. On the other hand, the suction opening 30 which attracts the inside of the tubed tumbler 22 is formed in the center of upper limit, and this suction opening 30 is connected to the vacuum aspirator which is not illustrated. In addition, the upper limit side of the tubed tumbler 22 is constituted so that it can open and close.

[0078] The same organic solvent as the organic solvent of the paste for electrode catalyst bed formation is first introduced from an inlet 28, and the inside of the tubed tumbler 22 is filled with the thin film-ized production process using this thin film deposition system 20 with the organic solvent of maximum vapor tension. Thereby, the inside of the tubed tumbler 22 serves as the environment where the organic solvent in a paste does not volatilize, even if the paste for electrode catalyst bed formation is introduced. And the paste 32 for electrode catalyst bed formation is introduced from an inlet 28, rotating this tubed tumbler 22, and the tubed tumbler 22 is rotated for 20 minutes with the rotational speed which requires the centrifugal force of 20G (G is gravitational acceleration). Between rotations of this tubed tumbler 22, the paste 32 for electrode catalyst bed formation is delayed in the shape of a film along with the Teflon sheet 26 of tubed tumbler 22 inner circle wall in response to centrifugal force. And the catalyst support carbon in the paste 32 for electrode catalyst bed formation receives this centrifugal force too, and sediments to the Teflon sheet 26 side compulsorily. By this compulsory sedimentation, the laminating of the catalyst support carbon is carried out to the Teflon sheet 26 side in the inside of a short time, and the axis-of-rotation side of the tubed tumbler 22 serves as a supernatant with which a fluorine system sulfonic-acid macromolecule resin solution exists. That is, sedimentation of the catalyst support carbon in the standing production process of the 1st example shown in drawing 3 takes place promptly according to this thin film-ized production process.

[0079] Then, while continuing rotation of the tubed tumbler 22 and heating the inside of the tubed tumbler 22 at 50 degrees C at a heater 24 in the meantime, vacuum suction of the inside of the tubed tumbler 22 is carried out through the suction opening 30. That is, the film formation production process of having a vacuum drying is performed following the thin film-ized production process of the tubed tumbler 22 which is made to carry out high-speed rotation and makes a paste the shape of a film. This thin film production process is different from the thin film production process of the 1st example in that a vacuum drying is performed during rotation of the tubed tumbler 22. If this thin film production process is followed, it passes through the same production process as the 1st example. However, on the occasion of adhesion with the electrolyte film 10 which passed through the hotpress, it is stuck to the film surface of the side located during rotation of the tubed tumbler 22 at the axis-of-rotation side with the electrolyte film 10.

[0080] Therefore, even if it is the fuel cell of this 4th example, like the 1st example, by the electrolyte film side of an electrode catalyst bed, there are many amounts of polyelectrolytes, the opening between catalyst support carbon is small, there are few amounts of polyelectrolytes at an electrode side, and the opening between catalyst support carbon becomes large. For this reason, also with the fuel cell of the 4th example, the use effectiveness of the catalyst in an electrode catalyst bed can be raised, electrode reaction can be made more smoothly and active, and the cell engine performance can be improved further.

[0081] Moreover, while the cell voltage higher than the example fuel cell of a comparison about each current density was obtained also by the fuel cell of this 4th example so that clearly from the data about the fuel cell of the 4th example in a table 1, even if it was a high current density field, the use effectiveness of the catalyst in an electrode catalyst bed was maintainable.

[0082] Furthermore, since catalyst support carbon is compulsorily sedimented according to centrifugal force, sedimentation is made to complete to the inside of a short time in this 4th example. Therefore, according to the manufacturing process of the 4th example, the fuel cell which has the high cell engine performance can be manufactured to the inside of a short time only by taking the simple production process of doing centrifugal force within the tubed tumbler 22. And since catalyst support carbon is sedimented according to centrifugal force, this sedimentation can be caused, without being influenced

by the rheology of the difficult paste of preparation. Therefore, preparation of the rheology of a paste becomes unnecessary and can attain simplification of a manufacturing process. In addition, according to the manufacturing process of the 4th example, equalization of the thickness of the cathode lateral electrode catalyst bed 12 and the anode lateral electrode catalyst bed 14 can also be attained through equalization of the thin film of the paste 32 for electrode catalyst bed formation formed along with the Teflon sheet 26 of tubed tumbler 22 inner circle wall. Moreover, improvement in the yield of the paste for electrode catalyst bed formation can also be aimed at.

[0083] Next, the fuel cell of the 5th example is explained. With the fuel cell of this 5th example, it differs from the 4th example in the preparation production process of that manufacturing process the point of preparing the paste for electrode catalyst bed formation using a superfluous fluorine system sulfonic-acid macromolecule resin solution and a superfluous organic solvent, and in that the electrolyte film 10 as an independent configuration member is not used.

[0084] that is, -- the preparation production process of this 5th example -- platinum (mean particle diameter of about 1nm) -- 20wt(s)% -- 100ml weighing capacity of the propylene glycol is carried out for a fluorine system sulfonic-acid macromolecule resin solution (solution with which the solid content of the resin concerned was blended at 5wt(s)% as 150ml and an organic solvent to supported catalyst support carbon (mean particle diameter of about 20nm) 1g. And the catalyst support carbon, fluorine system sulfonic-acid macromolecule resin solution, and organic solvent of only a required amount were prepared by this ratio, and the fluorine system sulfonic-acid macromolecule resin solution prepared the superfluous paste for electrode catalyst bed formation.

[0085] After that, like the 4th example, the thin film-ized production process and film formation production process using a thin film deposition system 20 were performed, and the thin film was formed from the paste for electrode catalyst bed formation. In this case, at the thin film-ized production process, the tubed tumbler 22 was rotated for 120 minutes with the rotational speed which requires the centrifugal force of 30G. In the paste delayed in the shape of a film between thin film-ized production processes, on the laminating of catalyst support carbon, a lot of supernatants remained and the thin film was formed through the film formation production process in this 5th example in this condition. In addition, in the film formation production process, the vacuum drying was performed at 100 degrees C.

[0086] In this way, even if it is the formed thin film, there are few amounts of polyelectrolytes at the Teflon sheet side in the case of a thin film-ized production process, and the opening between catalyst support carbon becomes large. Moreover, there are many amounts of polyelectrolytes and the opening between catalyst support carbon becomes small as it separates from a Teflon sheet side. And in a Teflon sheet and the opposite side (axis-of-rotation side of the tubed tumbler 22), the field of only fluorine system sulfonic-acid macromolecule resin (the amount of polyelectrolytes) is formed on the laminating of catalyst support carbon.

[0087] In the 5th example, after passing through a thin film-ized production process and a film formation production process, the following production process is performed. First, two thin films formed from the above-mentioned paste for electrode catalyst bed formation through the thin film-ized production process and the film formation production process are prepared. And the field of only a polyelectrolyte is formed in this thin film of two sheets, near film surfaces are stuck, and a hotpress (126 degree-Cx100 kg/cm<sup>2</sup>) is carried out. In this way, the electrode catalyst structure which has the electrode catalyst bed in which catalyst support carbon carried out the laminating on both sides was obtained. In this electrode catalyst structure, the cast film which is about 50 micrometers which the field of only a polyelectrolyte joined was formed in that center. After that, removed the Teflon sheet, pinched the electrode catalyst structure with the cathode 50 and the anode 52, these were made to unify, and the fuel cell was completed.

[0088] In the fuel cell of this 5th example, since the cast film which the field of only a polyelectrolyte comes to join in the center of the electrode catalyst structure has the thickness of about 50 micrometers, this cast film can be used as substitution of the electrolyte film 10. And like each above-mentioned example, there are few amounts of polyelectrolytes, the opening between catalyst support carbon becomes large, by the cast film side, there are many amounts of polyelectrolytes and the opening

between catalyst support carbon becomes small at an electrode side. Therefore, even if it is the fuel cell of this 5th example, like each above-mentioned example, the use effectiveness of the catalyst in an electrode catalyst bed can be raised, electrode reaction can be made more smoothly and active, and the cell engine performance can be improved further.

[0089] In the fuel cell of this 5th example, since the cast film equivalent to an electrolyte film is formed in the thin film, the resistance as an electrolyte film can be lowered. For this reason, in the fuel cell of the 5th example, the fall of the output voltage in a high current density field can be controlled further.

[0090] Moreover, while the cell voltage higher than the example fuel cell of a comparison about each current density was obtained also by the fuel cell of this 5th example so that clearly from the data about the fuel cell of the 5th example in a table 1, even if it was a high current density field, the use effectiveness of the catalyst in an electrode catalyst bed was maintainable.

[0091] Furthermore, in this 5th example, since the cast film of the center of the electrode catalyst structure is used as substitution of the electrolyte film 10, it is not necessary to prepare the electrolyte film 10 according to an individual. For this reason, in the 5th example, about the configuration of a fuel cell and its manufacturing process can also be simplified.

[0092] Next, the fuel cell of the 6th example is explained. In the fuel cell of this 6th example, the fuel cell cellular structure is the same as the 1st example. However, the cathode lateral electrode catalyst bed 12 and the anode lateral electrode catalyst bed 14 are different from the 1st example described above at the point which is the three-tiered structure in which the 1st - the 3rd catalyst bed carried out the laminating, respectively. The fuel cell of the 6th example which has the electrode catalyst bed of such a three-tiered structure is manufactured through the following manufacturing processes.

[0093] First, the paste for the 1st catalyst bed formation for forming the 1st catalyst bed is prepared, namely, platinum (mean particle diameter of about 1nm) - 20wt(s)% - 15ml weighing capacity of the fluorine system sulfonic-acid macromolecule resin solution (solution with which the solid content of the resin concerned was blended at 5wt(s)% is carried out to supported catalyst support carbon (mean particle diameter of about 20nm) 1g. Furthermore, weighing capacity of ethylene glycol mono-isopropyl ether and every 5ml of the isopropanols is carried out as an organic solvent, respectively. And the paste for the 1st catalyst bed formation is prepared through ultrasonic distribution in the well-closed container of these raw materials. Similarly, the paste for the 2nd catalyst bed formation and the paste for the 3rd catalyst bed formation are prepared. Under the present circumstances, in the paste for the 2nd catalyst bed formation, by 10ml and the paste for the 3rd catalyst bed formation, 5ml weighing capacity of the fluorine system sulfonic-acid macromolecule resin solution is carried out to catalyst support carbon 1g to catalyst support carbon 1g, and fluorine system sulfonic-acid macromolecule resin solutions are a paste for the 1st catalyst bed formation, and tales doses about an organic solvent. That is, in each paste for formation of the 3rd of the 1st - a catalyst bed, the amounts of fluorine system sulfonic-acid macromolecule resin solutions to catalyst support carbon differ, and the amount of fluorine system sulfonic-acid macromolecule resin solutions decreases in order of the paste for the 1st catalyst bed formation, the paste for the 2nd catalyst bed formation, and the paste for the 3rd catalyst bed formation.

[0094] Next, the paste printed matter of homogeneity thickness is obtained from each paste which carried out [ above-mentioned ] preparation with a doctor blade on a Teflon sheet like the 1st example. In this case, that thickness was set to 50 micrometers in the paste printed matter from the paste for the 1st catalyst bed formation, and the paste for the 3rd catalyst bed formation, and it could be 100 micrometers in the paste printed matter from the paste for the 2nd catalyst bed formation. In this obtained paste printed matter, the amount of fluorine system sulfonic-acid macromolecule resin in paste printed matter (the amount of polyelectrolytes) decreases in the order of the paste for the 1st catalyst bed formation, the paste for the 2nd catalyst bed formation, and the paste for the 3rd catalyst bed formation.

[0095] After that, each obtained paste printed matter is immediately given to ordinary temperature desiccation, and it carries out on a vacuum drying at 50 degrees C. The thin film the catalyst support carbon covered with the fluorine system sulfonic-acid macromolecule resin which is a polyelectrolyte by this carried out [ the thin film ] the laminating is formed, respectively. Subsequently, the laminating of each thin film is carried out to the electrolyte film 10 at order with many amounts of fluorine system

sulfonic-acid macromolecule resin to catalyst support carbon. That is, the hotpress (126 degree-Cx100 kg/cm<sup>2</sup>) of the thin film formed through paste printed matter from the paste for the 1st catalyst bed formation is first stuck and carried out to the electrolyte film 10. Next, a Teflon sheet is removed from a thin film [ finishing / this press ], and the hotpress of the thin film [ finishing / formation ] is stuck and carried out to the thin film after sheet removal from the paste for the 2nd catalyst bed formation.

Similarly, the hotpress of the thin film [ finishing / formation ] is stuck and carried out to the thin film after sheet removal from the paste for the 3rd catalyst bed formation.

[0096] Thereby, each thin film serves as the 1st - the 3rd catalyst bed, and the electrode catalyst bed (the cathode lateral electrode catalyst bed 12, anode lateral electrode catalyst bed 14) of the three-tiered structure in which these carried out the laminating is formed. And the cathode 50 and the anode 52 were pressed in this two-electrodes catalyst bed, these were unified, and the fuel cell (cel) was completed. In addition, each above-mentioned thin film is beforehand cut out by electrode size in advance of a hotpress.

[0097] In the fuel cell of this 6th example, the amount of polyelectrolytes has decreased in order of the 1st, 2nd, and 3rd catalyst bed. Therefore, like each above-mentioned example, by the 1st catalyst bed by the side of an electrolyte film, there are many amounts of polyelectrolytes, the opening between catalyst support carbon is small, there are few amounts of polyelectrolytes at the 3rd catalyst bed by the side of an electrode, and the opening between catalyst support carbon becomes large. For this reason, also with the fuel cell of the 6th example, the use effectiveness of the catalyst in an electrode catalyst bed can be raised, electrode reaction can be made more smoothly and active, and the cell engine performance can be improved further.

[0098] Moreover, while the cell voltage higher than the example fuel cell of a comparison about each current density was obtained also by the fuel cell of this 6th example so that clearly from the data about the fuel cell of the 6th example in a table 1, even if it was a high current density field, the use effectiveness of the catalyst in an electrode catalyst bed was maintainable.

[0099] Although the example of this invention was explained above, as for this invention, it is needless to say that it can carry out in the mode which becomes various in the range which is not limited to such an example at all and does not deviate from the summary of this invention.

[0100] For example, it is good also as the paste for electrode catalyst formation which used the paste for electrode catalyst formation used at the thin film-sized production process in the 4th above-mentioned example in the 2nd and 3rd example, i.e., a paste which mixed and distributed different catalyst support of particle size. Thus, with constituting, the production time of an electrode catalyst bed, as a result a fuel cell can be shortened.

[0101] Moreover, in the 5th example, by supporting the catalyst support carbon with the mean particle diameter smaller than usual catalyst support carbon (mean particle diameter of 20-40 micrometers) to the paste for electrode catalyst formation, for example, a platinum catalyst, you may constitute so that little combination of the catalyst support carbon the mean particle diameter of whose is 1-5 micrometers may be carried out. thus, when constituted, in a thin film-sized production process, sedimentation of the catalyst support carbon of this detailed particle size is delayed for usual catalyst support carbon, and is cut. That is, the catalyst support carbon of detailed particle size is in the process of sedimentation also after the completion of sedimentation of usual catalyst support carbon. For this reason, the catalyst support carbon of detailed particle size can use the cast film of the center of the electrode catalyst structure as the cast film which carried out the little residual.

[0102] Therefore, even if fuel gas carries out crossing leak at the electrode side which counters from a cathode 50 or an anode 52, electrode reaction can be presented with this fuel gas in the electrode catalyst structure according to the catalyst in the catalyst support carbon of the detailed particle size in a cast film. Therefore, it can avoid that the reaction (reaction of hydrogen and oxygen) of fuel gas occurs by the electrode catalyst structure, and the unprepared heat damage of a cast film can be prevented. Moreover, this cast film can be made humid with the generation water generated according to electrode reaction, and hydrogen ion diffusion of the film concerned is not checked.

[0103] Moreover, in the 6th example, although the electrode catalyst bed was made into the three-tiered

structure which carried out the laminating of the 1st, 2nd, and 3rd catalyst bed, it can also be made into two-layer structure or the structure of four or more layers.

[0104] Furthermore, in each above-mentioned example, on the occasion of preparation of the paste for electrode catalyst bed formation, catalyst support carbon was only merely mixed with the fluorine system sulfonic-acid macromolecule resin solution (polyelectrolyte solution) to the organic solvent, and ultrasonic distribution of these was carried out. However, generally, carbon has hydrophobicity and fluorine system sulfonic-acid macromolecule resin has hydrophilicity by the own sulfone radical. For this reason, when ultrasonic distribution is inadequate, catalyst support carbon is condensed with carbon with a mutual property, and there is a possibility that it may become inadequate fluorine system sulfonic-acid macromolecule resin covering [ of catalyst support carbon ] (polyelectrolyte covering). Therefore, in order to aim at positive covering of the catalyst support carbon by the polyelectrolyte, as it is the following, it is desirable to prepare the paste for electrode catalyst bed formation.

[0105] For example, the catalyst support carbon which a polyelectrolyte solution is made to mix is used as the carbon which the basic functional group combined with the surface aromatic series ring, or it considers as the carbon charged in positive charge. Since it is as follows and condensation of catalyst support carbon will not occur if it does in this way, positive covering of the catalyst support carbon by the polyelectrolyte can be aimed at.

[0106] With the catalyst support carbon which the basic functional group combined with the surface aromatic series ring, the basic functional group combined with the surface aromatic series ring changes to a cation in a solution. For this reason, catalyst support carbon of condense [ oppose electrically suit and / in a polyelectrolyte solution ] decreases. And since a polyelectrolyte has a negative ion exchange group (for example, sulfone radical) to a hydrogen ion (cation), catalyst support carbon pays well on a polyelectrolyte and an electrochemistry target. Consequently, each catalyst support carbon is certainly covered in the paste for electrode catalyst bed formation prepared using the catalyst support carbon which the basic functional group combined with the surface aromatic series ring by the polyelectrolyte.

[0107] On the other hand, the catalyst support carbon of each other which electrified positive charge is electrically repelled with the electrification charge, and condense [ suit and ] decreases. And it pays well on the polyelectrolyte and electrochemistry target which have a negative ion exchange group. Consequently, even if it is the paste for electrode catalyst bed formation prepared using the catalyst support carbon which electrified positive charge, each catalyst support carbon is certainly covered with a polyelectrolyte.

[0108] And if such catalyst support carbon is used, since each catalyst support carbon is certainly covered with the polyelectrolyte, through change of the amount of polyelectrolytes, more certainly, diffusional permeability of reactant gas will be made in an electrode side, and conductivity of a hydrogen ion can be highly made high in an electrolyte film side.

[0109] In addition, what is necessary is just to perform association of the basic functional group to the surface aromatic series ring of catalyst support carbon as follows. First, a catalyst support carbon particle is heat-treated with a nitric acid (HNO<sub>3</sub>) (heating temperature: about 400 degrees C), and the surface aromatic series ring of carbon is nitrated (-NO<sub>2</sub>). Subsequently, using nickel as a reduction catalyst, this nitro group (-NO<sub>2</sub>) is returned from hydrogen, and it replaces by the amino group (-NH<sub>2</sub>). In this way, the amino group (-NH<sub>2</sub>) which is a basic functional group is combined with the surface aromatic series ring of catalyst support carbon. This amino group (-NH<sub>2</sub>) is ionized in a solution, and changes to a cation (ammonium ion).

[0110] Moreover, what is necessary is just to perform electrification of the positive charge to catalyst support carbon as follows using the paste preparation equipment 60 shown in drawing 7. First, a catalyst support carbon particle is put into the positive charge electrification room 62 of paste preparation equipment 60. Here, paste preparation equipment 60 is explained in advance of explanation of electrification of positive charge.

[0111] Paste preparation equipment 60 is equipped with the positive charge electrification room 62 and the negative charge electrification room 66 on both sides of a dielectric 64. And if a switch 68 is closed by the electrode boards 62a and 66a of each electrification interior of a room, positive and negative

charge will be built over them in response to the charge of DC power supply 70. The positive charge electrification room 62 is sealed and has entry bulb 62b for putting in catalyst support carbon and a fluorine system sulfonic-acid macromolecule resin solution, and draining valve 62c for discharging an enclosure object.

[0112] After putting catalyst support carbon into the positive charge electrification room 62 from entry bulb 62b, a switch 68 is closed and positive charge is covered for electrode board 62a in the positive charge electrification room 62. Thereby, at the positive charge electrification room 62, catalyst support carbon is charged in positive charge.

[0113] In this way, in the condition that catalyst support carbon is charged in positive charge, a polyelectrolyte solution and an organic solvent are put in from entry bulb 62b, respectively. And an ultrasonic wave is emitted to the positive charge electrification room 62 from the ultrasonic horn which is not illustrated, and a polyelectrolyte solution is made to carry out ultrasonic distribution of the catalyst support carbon with which positive charge was charged.

[0114]

[Effect of the Invention] As explained in full detail above, with claim 1 and the fuel cell according to claim 6, the opening between the catalyst support in an electrode catalyst bed was enlarged by the electrode side, diffusional permeability of reactant gas was made high by the electrode side, the amount of polyelectrolytes was made [ many ] by the electrode and solid-state polyelectrolyte film side of the opposite side, and conductivity of a hydrogen ion was made high by the solid-state polyelectrolyte film side. Therefore, at an electrode catalyst bed, while the diffusion rate of reactant gas increases by the electrode side, the electric conduction speed of a hydrogen ion increases by the electrode and solid-state polyelectrolyte film side of the opposite side. Consequently, according to claim 1 and the fuel cell according to claim 6, the use effectiveness of the catalyst in an electrode catalyst bed can be raised, electrode reaction can be made more smoothly and active, and the cell engine performance can be improved further.

[0115] Moreover, according to the manufacture method of claim 2 thru/or claim 5, and a fuel cell according to claim 7, the fuel cell which has the high cell engine performance can be manufactured only by taking simple production processes, such as standing of the prepared mixed solution, a centrifugal operation to a mixed solution, or a laminating of two or more thin films.

[0116] According to the manufacture method of a fuel cell according to claim 3, the production time can be shortened.

[0117] According to the manufacture method of a fuel cell according to claim 4, the opening between catalyst support can be made small, so that the bottom side separates the opening between catalyst support from a bottom greatly in the laminating of catalyst support itself. Therefore, in an electrode catalyst bed, the conductivity of a hydrogen ion can manufacture a fuel cell with the more high diffusional permeability of reactant gas by the electrode side highly more by the solid-state polyelectrolyte film side.

[0118] In a fuel cell according to claim 6, since a solid-state polyelectrolyte film is not needed, about the configuration of a fuel cell and its manufacturing process can also be simplified.

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[Translation done.]

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## CLAIMS

## [Claim(s)]

[Claim 1] An electrode catalyst bed which comes to carry out the laminating of the catalyst support is stuck on a solid-state polyelectrolyte film which has the permselectivity of a hydrogen ion. It is the fuel cell which this electrode catalyst bed was made to intervene and pinched this solid-state polyelectrolyte film with an electrode of the gaseous diffusion nature of a pair. Said electrode catalyst bed Come to carry out the laminating of the catalyst support covered with a polyelectrolyte which has the permselectivity of a hydrogen ion, and an opening between catalyst support in said electrode catalyst bed A fuel cell characterized by being made larger than said solid-state polyelectrolyte film side at said electrode side by changing said amount of polyelectrolytes which covers said catalyst support along the direction of a laminating of said catalyst support.

[Claim 2] A manufacture method of a fuel cell according to claim 1 characterized by providing the following A preparation production process for which a mixed solution of said catalyst support and said polyelectrolyte solution, and an volatile organic solvent is prepared A standing production process which puts this mixed solution on environment where extend in the shape of a thin film, and said volatile organic solvent does not volatilize, gently [ time amount to which said catalyst support can sediment ] A film formation production process which forms a thin film through desiccation processing from a mixed solution extended in the shape of [ said ] a thin film An adhesion production process which sticks a formed this thin film to said solid-state polyelectrolyte film so that a film surface of a side which had become the upper surface at the time of said standing may join to a film surface of said solid-state polyelectrolyte film

[Claim 3] A manufacture method of a fuel cell according to claim 1 characterized by providing the following A preparation production process for which a mixed solution of said catalyst support and said polyelectrolyte solution, and an volatile organic solvent is prepared A thin film-ized production process which puts this mixed solution into a tumbler which is put on environment where said volatile organic solvent does not volatilize, and rotates, exerts centrifugal force on this intrusion rare \*\*\*\*, and extends this mixed solution in the shape of a thin film A film formation production process which forms a thin film through desiccation processing from a mixed solution extended in the shape of [ said ] a thin film An adhesion production process which sticks a formed this thin film to said solid-state polyelectrolyte film so that a film surface of a side which had turned into the inside within a tumbler at the time of rotation of said tumbler may join to a film surface of said solid-state polyelectrolyte film

[Claim 4] It is the manufacture method of a fuel cell according to claim 2 or 3, and a preparation production process according to claim 2 or 3 is a production process for which a mixed solution of at least two or more catalyst support from which particle size differs, said polyelectrolyte solution, and an volatile organic solvent is prepared.

[Claim 5] A manufacture method of a fuel cell according to claim 1 characterized by providing the following A production process for which said catalyst support and said polyelectrolyte solution, and an volatile organic solvent are mixed, and two or more mixed solutions with which said amounts of polyelectrolytes to said catalyst support differ are prepared this -- a production process which forms two

or more thin films with which said amounts of polyelectrolytes to said catalyst support differ using two or more mixed solutions A production process which carries out the laminating of the two or more formed this thin films to said solid-state polyelectrolyte film at order with many said amounts of polyelectrolytes to said catalyst support

[Claim 6] An electrode catalyst bed which comes to carry out the laminating of the catalyst support, and an electrode of gaseous diffusion nature are stuck, and it is the fuel cell which it has a pair every. Said electrode catalyst bed Come to carry out the laminating of the catalyst support covered with a polyelectrolyte which has the permselectivity of a hydrogen ion, and an opening between catalyst support in said electrode catalyst bed By changing said amount of polyelectrolytes which covers said catalyst support along the direction of a laminating of said catalyst support, it is the fuel cell which is enlarged by said electrode side and characterized by joining an electrode catalyst bed of said pair so that sides with a small opening between said catalyst support may stick.

[Claim 7] A manufacture method of a fuel cell according to claim 6 characterized by providing the following A preparation production process according to claim 2 or 3 A production process of either a standing production process according to claim 2 or a thin film-sized production process according to claim 3 A film formation production process according to claim 2 or 3 One cementation production process of the cementation production processes which make stick the film surfaces of the side which had turned into the inside within a tumbler in said thin film-sized production process in the thin film of the cementation production process which is made to stick the film surfaces of a side which had become the upper surface in said standing production process at the time of standing about a production process which carries out pair preparation of the formed this thin film, and a thin film of a this prepared pair, and is joined, and the this prepared pair, and join

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[Translation done.]

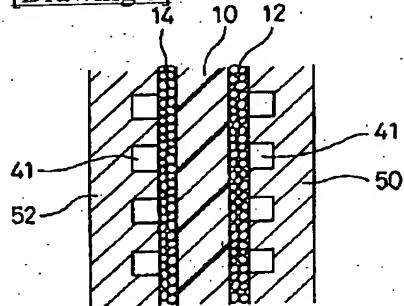
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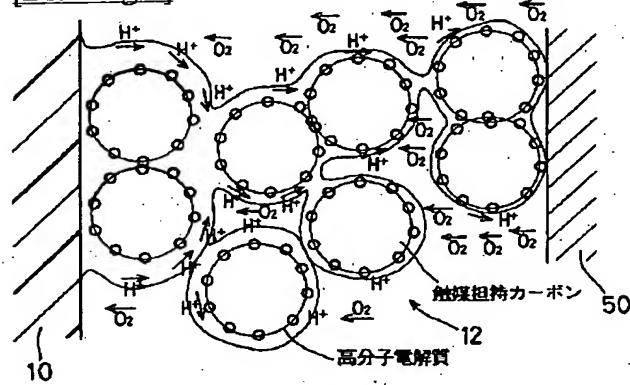
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## DRAWINGS

[Drawing 1]

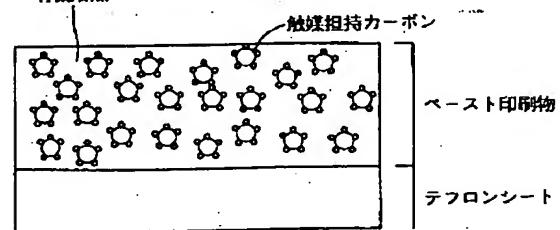


[Drawing 4]

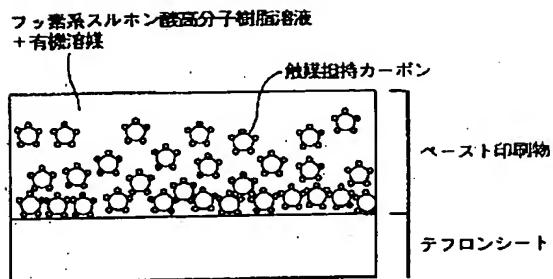


[Drawing 2]

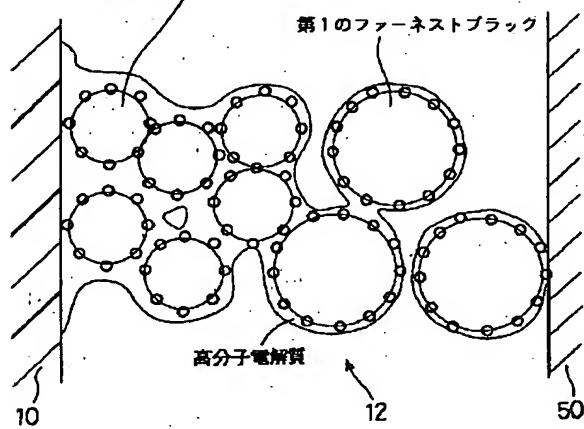
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+有機溶媒



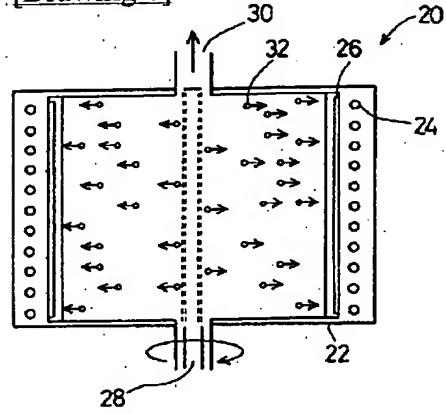
[Drawing 3]



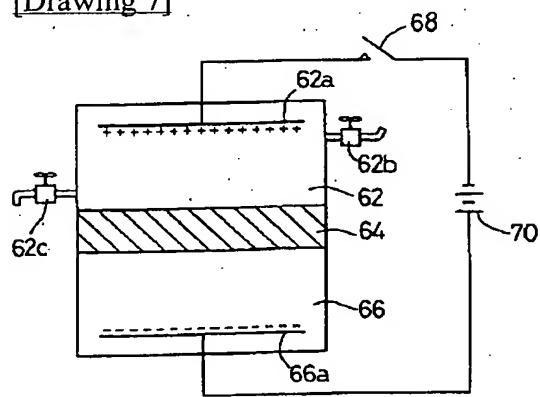
[Drawing 5]  
第2のファーネストブラック



[Drawing 6]



[Drawing 7]



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[Translation done.]